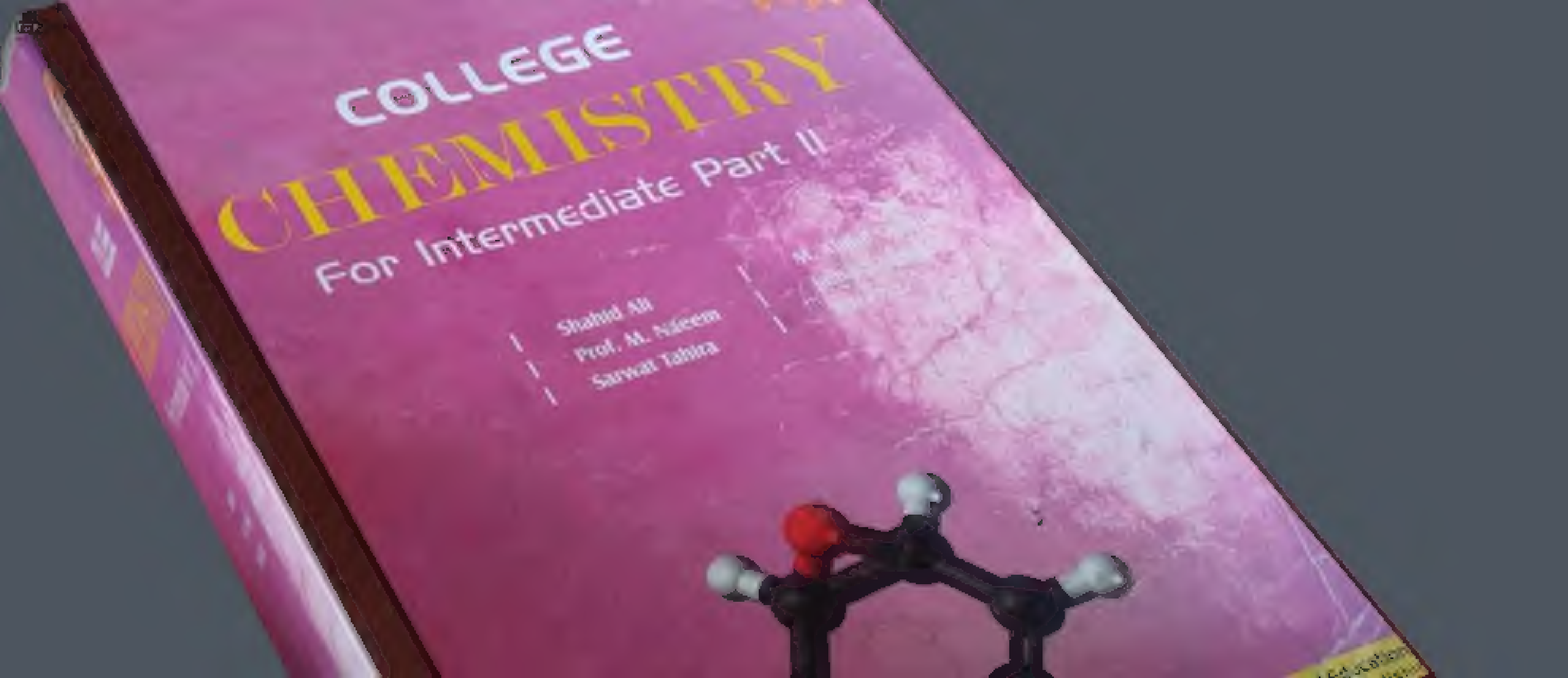
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CHEMISTRY
For Intermediate Part II
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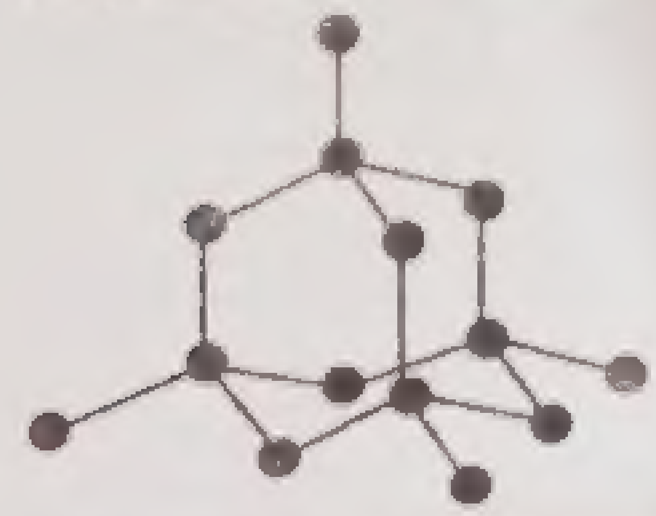
CHAPTER # 13

s and p-BLOCK ELEMENTS



PERIOD 3 (Na to Ar)

ATOMIC AND PHYSICAL PROPERTIES OF THE PERIOD 3 ELEMENTS

This period contains Sodium (Na), Magnesium (Mg), Aluminum (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar).

(A) ATOMIC PROPERTIES

(1) ELECTRONIC STRUCTURES

In Period 3 of the Periodic Table, the valence orbtials are 3s and 3p orbitals. They are filled with electrons. The short electronic structures are:

$_{11}Na$	$[Ne]\ 3s^1$
$_{12}Mg$	$[Ne]\ 3s^2$
$_{13}Al$	$[Ne]\ 3s^2\ 3p_x^1$
$_{14}Si$	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1$
$_{15}P$	$[Ne]\ 3s^2\ 3p_x^1\ 3p_y^1\ 3p_z^1$
$_{16}S$	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$
$_{17}Cl$	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$
$_{18}Ar$	$[Ne]\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$

In each case, [Ne] represents the complete electronic structure of a neon atom. (i.e. 10 electrons)

QUICK QUIZ-1

(1) The electron structure of Mg is $1s^2, 2s^2, 2p^6, 3s^2$. Write down electron structure of Al in the same notation.

$_{13}Al\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

√ ***(2) Which of the two elements Mg or Al has the more stable structure?***

Mg has more stable structure. It is because it has completely filled 3s-valence orbital (i.e. $3s^2$). On the other hand Al has one valence electron in 2p-orbital which can be easily removed. Hence, Mg has more stable electronic structure. This is also indicated by high first ionization energy of Mg than that of Al.

(2) TRENDS IN ATOMIC RADIUS

- ***The distance of outermost electron from the nucleus of an atom while considering it spherical is called atomic radius.***
- ***The size of atoms and ions decreases from left to right along the period.*** In a given period, the number of shells in all the elements remains the same. However, the value of effective nuclear charge increases from left to right due to increase in number of protons. The increased effective nuclear charge pulls the electron cloud of the atom closer to the nucleus. Thus, the size of the atoms and ions goes on decreasing from left to right.
- Along period the atomic and ionic radii of s-and p-block elements decrease with the increase of atomic number. This is shown in the table given below. The radii in the table are given in Å

Group → / Period ↓	s-Block elements		p-Block elements				
	I A	II A	III A	IV A	V A	VI A	VII A
1	H 2.08 (-1) 0.29 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3)	C 2.60 (-4) 0.15 (+4)	N 1.71 (-3) 0.11 (+5)	O 1.40 (-2) 0.09 (+6)	F 1.36 (-1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (-4) 0.41 (+4)	P 2.12 (-3) 0.34 (+5)	S 1.84 (-2) 0.29 (+6)	Cl 1.81 (-1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (-3) 0.47 (+5)	Se 1.98 (-2) 0.42 (+6)	Br 1.95 (-1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 2.45 (-3) 0.62 (+5)	Te 2.21 (-2) 0.56 (+6)	I 2.16 (-1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Tl 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po	At
7	Fr 1.76 (+1)	Ra 1.40 (+2)					

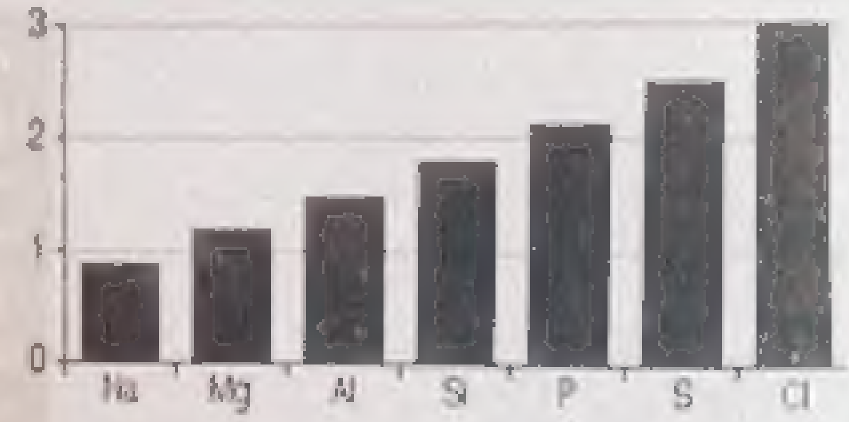
(3) TRENDS IN ELECTRONEGATIVITY

Definition

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

Scale of Electronegativity

- The Pauling scale is the most commonly used.
- Fluorine is the most electronegative element. It is assigned a value of 4.0.
- The values range down to caesium and francium which are the least electronegative at 0.7.



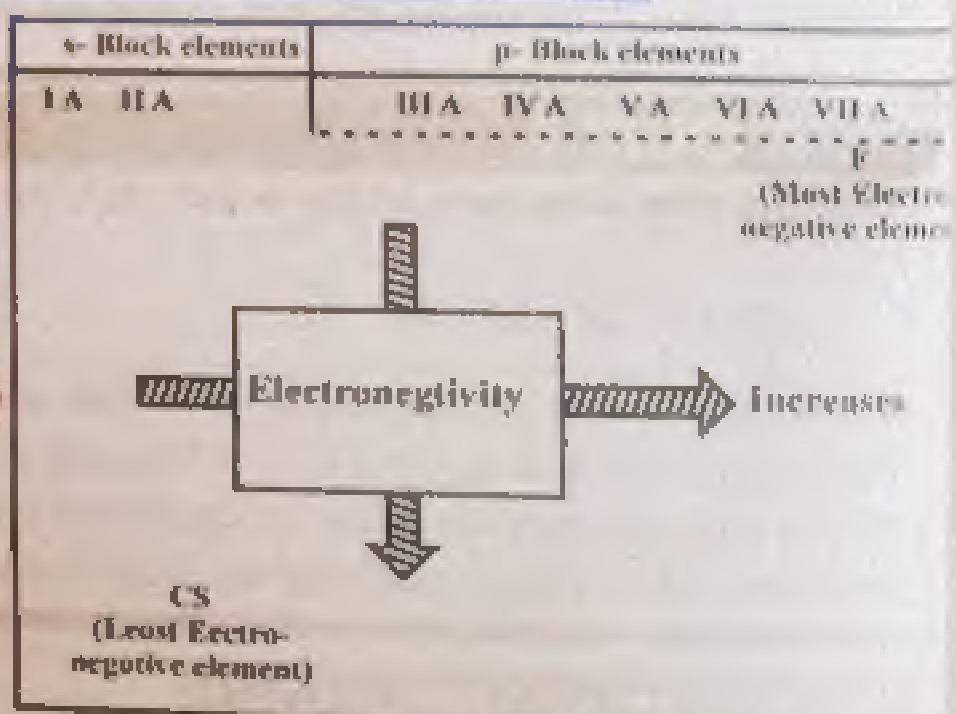
Trend or Variation in electronegativity along period:

The electronegative values increases from left to right in a period of s- and p-block elements.

It is due to following reasons.

(i) In a period, the atomic size decreases from left to right. Since, smaller atoms have greater tendency to attract the electrons towards themselves. Thus, smaller atoms have higher electronegativity values.

(ii) In a period, values of ionization energy and electron affinity of the elements increase from left to right. Thus, the atoms of the elements with higher value of ionization energies and electron affinities also have higher electronegativities.



The variation of electronegativity in a period and a group of representative elements (s- and p-block elements) is show in the figure.

Electronegativity cannot be assigned to Argon

It is because electronegativity is the tendency of an atom to attract a **bonding pair** of electrons. Since argon does not form covalent bonds, electronegativity cannot be assigned to it.

Another Trend Explanation

- Along period from left to right, the bonding electrons are always in the same level. In period 3, it is the level ... Thus, they are always being shielded by the same inner electrons.
- However, the number of protons in the nucleus increases from left to right. Thus, due to increase in nuclear charge, it attracts the bonding pair more closely. Hence, electronegativity increase from left to right.

(B) PHYSICAL PROPERTIES

These properties depend upon the structure of elements.

STRUCTURES OF THE ELEMENTS

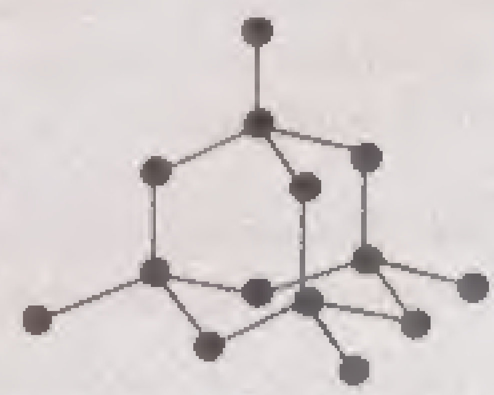
The structures of the elements changes along the period. In period 3, the first three (i.e. Na, Mg, Al) are metallic, silicon is giant covalent, and the remaining (i.e. P, S, Cl, Ar) are simple molecules.

(1) Three metallic structures

- Sodium, magnesium and aluminium all have metallic structures.
- In sodium, only one electron per atom is involved in the metallic bond **i.e.**, the single 3s electron. In magnesium, both of its outer electrons are involved. In aluminium all three valence electrons are involved.
- The other difference is the way of packing of atoms in the metal crystal.
  - ✓ Sodium is 8-co-ordinated. Thus, each sodium atom is touched by only 8 other atoms.
  - ✓ Both magnesium and aluminium are 12-co-ordinated. However, both are packed in slightly different ways. This is a more efficient way to pack atoms. Thus, there less space is wasted in the metal structures and therefore, stronger bonding is present in the metal.

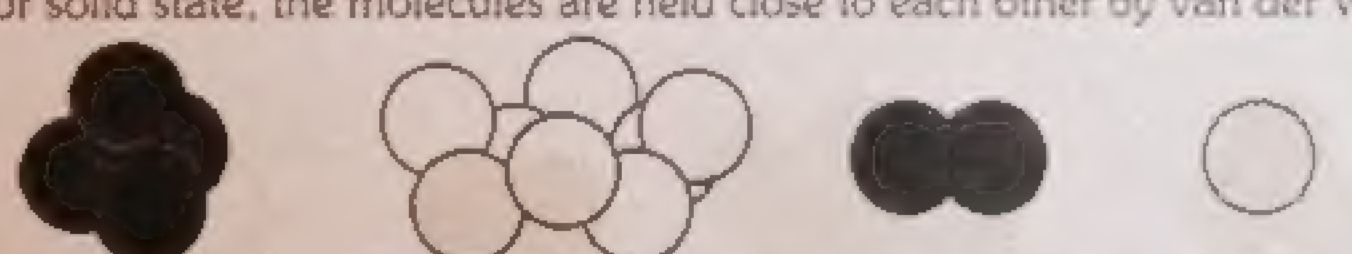
(2) A giant covalent structure

- Silicon has a giant covalent structure just like diamond as shown in the figure.
- The structure is held together by strong covalent bonds in all three dimensions.



(3) Four simple molecular structures

- The structures of phosphorus (i.e. white etc.) and sulphur (i.e. rhombic or monoclinic etc.) depends upon the allotropic forms of phosphorus or sulphur.
- The atoms in each of these molecules are held together by covalent bonds.
- In argon, there is no bond.
- In the liquid or solid state, the molecules are held close to each other by van der Waals dispersion forces.



a P_4 molecule an S_8 molecule a Cl_2 molecule an Ar molecule

(1) ELECTRICAL CONDUCTIVITY

- ***Sodium, magnesium and aluminium** are all good conductors of electricity.*

  Among these conductivity increases from left to right (i.e., from sodium to magnesium to aluminium).

  It is because, the number of valence (free) electrons increases. Sodium has one, magnesium has two and aluminium has three valence electrons.
- ***Silicon*** is a semiconductor.
- The rest elements of period 3 (***phosphorus, sulphur, chlorine and argon***) do not conduct electricity.

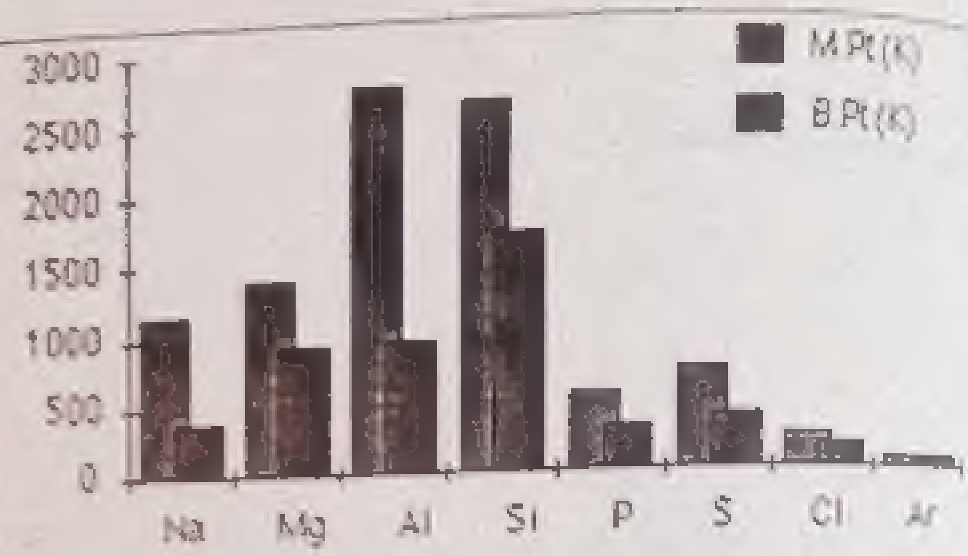
Explanation

- The three metals (Na, Mg, Al) conduct electricity. It is because the delocalized electrons (electrons sea) are free to move throughout the solid or the liquid metal.
- In the silicon case, the semiconductors conduct electricity depending upon conditions of temperature etc. Silicon has diamond like structure. So, it must be an insulator. But it is a semiconductor and its conductivity increases with increase in temperature.
- The remaining elements do not conduct electricity because they are simple molecular substances. They do not have free electrons to carry current.

Exercise Q3 (i) (d) The melting and boiling pints of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?

(2) TRENDS IN MELTING AND BOILING POINTS

- The figure shows the variation of melting and boiling points of the elements across the period 3.
- The melting and boiling points are given in Kelvin rather than °C to avoid negative values.



Sodium, Magnesium and Aluminium

They possess metallic structures. The melting point and boiling points increases from sodium to aluminium. It is because Na provides one valence electron for bonding, Mg provides two electrons and aluminium provides three electrons.

Silicon

- Silicon has high melting and boiling points because it is a giant covalent structure. It has strong covalent bonds which are difficult to break.
- Since silicon has a different type of bonds so its melting and boiling points should not be directly compare with that of aluminium.

The Four Molecular Elements

- Phosphorus, sulphur, chlorine and argon are simple molecular substances.
- These have only weak van der Waals forces between the molecules. Hence, their melting or boiling points are lower than those of the first four members of the period which have giant structures.
- The sizes of the melting and boiling points depends upon the sizes of the molecules. Generally, the melting and boiling points increase with increase in molecular size.

Phosphorus

Phosphorus consists of P_4 molecules. To melt phosphorus there is no need to break any covalent bonds. Only much weaker van der Waals forces between the molecules are broken. Thus, its melting point is low.

Sulphur

Sulphur consists of S_8 rings of atoms. So, its molecules are bigger (8 atoms) than phosphorus molecules (4 atoms). Hence, the van der Waals attractions will be stronger, leading to a higher melting and boiling point.

Chlorine

Chlorine, Cl_2, is a much smaller molecule with comparatively weak van der Waals attractions. Hence, chlorine will have a lower melting and boiling point than sulphur or phosphorus.

Argon

Argon molecules are just single argon atoms, Ar. They have limited and very weak van der Waals forces. Hence, the melting and boiling points of argon are lower again.

QUICK QUIZ-2

(a) *Write down the symbols of the elements in the third period of the periodic table (ending with the noble gas, argon) in order of increasing atomic number.*

The elements are: Sodium (Na), Magnesium (Mg), Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar).

(b) *Which of these elements are*

(i) *s-block elements:* Sodium (Na) and Magnesium. Since, both these have their valence electrons in s-orbital.

(ii) *p-block elements:* Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar). Since all these have their valence electrons in p-orbital.

(iii) *d-block elements:* There are no d-block elements in Period 3, since none of the period 3 elements have valence electron in d-orbital.

(c) (i) *Write the empirical formula of the chloride formed by the elements of atomic number 13.*

Element with atomic number 13 is Aluminum (Al). Thus the formula of its chloride is $AlCl_3$. However, it can exist in dimeric form, Al_2Cl_6, as well.

(ii) *Describe briefly how you could prepare a sample of this chloride.*

The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

(C) CHEMICAL REACTIONS OF THE PERIOD 3 ELEMENTS

The reactions of Period 3 elements are given below:

Exercise Q3 (i) (c): ***Describe the trends in reaction of period 3 elements with water.***

I) REACTIONS WITH WATER

Sodium

- Sodium has a very exothermic reaction with cold water producing hydrogen gas and a colourless solution of sodium hydroxide. The reaction is so much exothermic that the liberated hydrogen catches fire.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

Magnesium

- Magnesium has a very slight reaction with cold water, but burns in steam.
- A very clean coil of magnesium dropped into cold water finally gets covered in small bubbles of hydrogen which float it to the surface.
- Magnesium hydroxide is formed as a very thin layer on the magnesium. It acts as a protective layer and thus tends to stop the reaction.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

- Magnesium burns in steam with its typical white flame to produce white magnesium oxide and hydrogen.

$$Mg + H_2O \rightarrow MgO + H_2$$

Aluminium

- When Aluminium powder is heated in steam, it produces hydrogen and aluminium oxide.
- The reaction is relatively slow because of the strong aluminium oxide layer on the metal, and formation of more oxide during the reaction. The oxide layer acts as a protective layer and thus slows down the reaction.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$$

Phosphorus and sulphur

These have no reaction with water.

Chlorine

- Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to prod a mixture of hydrochloric acid and chloric(I) acid (hypochlorous acid).

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$

- In the presence of sunlight, the chloric(I) acid slowly decomposes to produce more hydrochloric acid, releas oxygen gas.

$$2HOCl \rightarrow 2HCl + O_2$$

- Thus overall reaction will be

$$2Cl_2 + 2H_2O \rightleftharpoons 2HCl + 2HOCl$$ (This equation is obtained by multiplying above equation with 2)

$$2HOCl \rightarrow 2HCl + O_2$$

$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$$

Argon

There is no reaction between argon and water

(2) REACTIONS WITH OXYGEN

Sodium

- Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sod peroxide

For the simple oxide

$$4Na + O_2 \rightarrow 2Na_2O$$

For the peroxide

$$2Na + O_2 \rightarrow Na_2O_2$$

Magnesium

Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.

$$2Mg + O_2 \rightarrow 2MgO$$

Silicon

Silicon will burn in oxygen if heated strongly. Silicon dioxide is produced.

$$Si + O_2 \rightarrow SiO_2$$

Phosphorus

- White phosphorus catches fire spontaneously in air. It burns with a white flame and producing clouds of w smoke which is a mixture of phosphorus(III) oxide and phosphorus(V) oxide.
  The proportions of two oxides depend on the amount of oxygen available.
- In an excess of oxygen, the product will be almost completely phosphorus (V) oxide.

For the phosphorus(III) oxide:

$$P_4 + 3O_2 \rightarrow \underset{\text{(phosphorus (III) oxide)}}{P_4O_6}$$

For the phosphorus(V) oxide:

$$P_4 + 5O_2 \rightarrow \underset{\text{(phosphorus (V) oxide)}}{P_4O_{10}}$$

Sulphur

- Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide g

$$S + O_2 \rightarrow SO_2$$

Chlorine and argon

- Despite having several oxides, chlorine won't react directly with oxygen. Argon does not react either.

Properties of the oxides of elements in Period 3

Formula of Oxide →	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (P_4O_6)	SO_3 (SO_2)	Cl_2O_7 (Cl_2O)
State of Oxide	solid	solid	solid	solid	solid	liquid	liquid
Conduction of Electricity by Molten or liquid Oxide	good	good	good	v poor	Nil	Nil	Nil
Structure of oxide	Giant Structures				Simple molecular structure		
Enthalpy change of Formation of oxide at 298K/kJ mol[-1]	–416	–602	–1676	–910	–2984	–395	80
Enthalpy change of Formation of oxide at 298K/kJ mol- kJ/kJ	–416	–602	–559	–455	–298	–132	80
Effect of adding oxide to water	reacts to form NaOH (aq) alkaline solution	reacts to form $Mg(OH)_2$	does not react with water but it is amphoteric	does not react with water but it is acidic	P_4O_{10} reacts to form H_3PO_4 (acid solution)	SO_3 reacts to form H_2SO_4 (acid solution)	Cl_2O_7 reacts to form $HClO_4$ (acid solution)
Nature of Oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

(3) REACTIONS WITH CHLORINE

Sodium

- Sodium burns in chlorine with a bright orange flame. White solid sodium chloride is produced.

$$2Na + Cl_2 \rightarrow 2NaCl$$

Magnesium

- Magnesium burns with its intense white flame to give white magnesium chloride.

$$Mg + Cl_2 \rightarrow MgCl_2$$

Aluminium

- Aluminium is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube.
- The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride. This sublimes (direct conversion from solid to vapour) and collects in the cooler part of the tube.

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Silicon

- When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride.
- $SiCl_4$ is a colourless liquid which vaporises and can be condensed further along the apparatus.

$$Si + 2Cl_2 \rightarrow SiCl_4$$

Phosphorus

- White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus(III) chloride and phosphorus(V) chloride (phosphorus trichloride, PCl_3 and phosphorus pentachloride, PCl_5).
- Phosphorus(III) chloride is a colourless fuming liquid.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

- Phosphorus(V) chloride is an off-white (going towards yellow) solid.

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

Sulphur

- When a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, evil-smelling liq... disulphur dichloride, S_2Cl_2.

$2S + Cl_2 \rightarrow S_2Cl_2$

Chlorine and Argon

- Chlorine gas (Cl_2) cannot react with itself.
- Argon does not react with chlorine.

(D) PHYSICAL PROPERTIES OF THE OXIDES

- The relationship between the physical properties of the oxides of Period 3 elements (sodium to chlorine) a... their structures is given below.
- Argon is omitted because it does not form an oxide.

THE OXIDES

The important oxides of Period 3 elements are:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
				P_4O_6	SO_2	Cl_2O

- Those oxides in the first row are known as the ***highest oxides*** of the various elements, **i.e.** In these oxides Period 3 elements are in their highest oxidation states.
- In highest oxides, all the valence electrons in the Period 3 element are involved in the bonding.

e.g. one electron for sodium, two for magnesium, three for aluminium and so on.

(i) STRUCTURES OF OXIDES

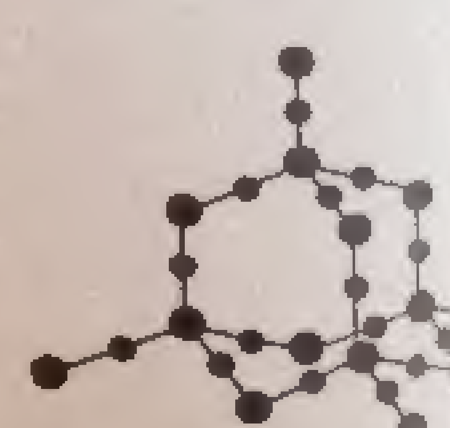
The trend in structure changes from the metallic oxides containing giant structures of ions on the left of period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

(I) The metallic oxides (e.g Sodium, Magnesium, aluminium etc.)

- Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride. i.e. They exi... ionic crystalline solids.

(II) Giant Covalent Oxides [e.g Silicon dioxide (silicon(IV) oxide)]

- Crystalline silicon has the same structure as diamond. In this structure atoms of both silicon and oxygen are present.
- In SiO_2, each silicon atom is bridged to its neighbouring silicon by an oxygen atom.



(III) The molecular oxides

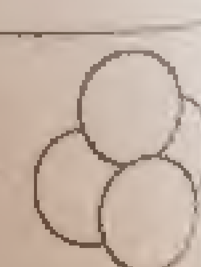
(e.g. Phosphorus, sulphur and chlorine oxides)

(A) THE PHOSPHORUS OXIDES

Phosphorus has two common oxides,

(I) Phosphorus(III) oxide, P_4O_6

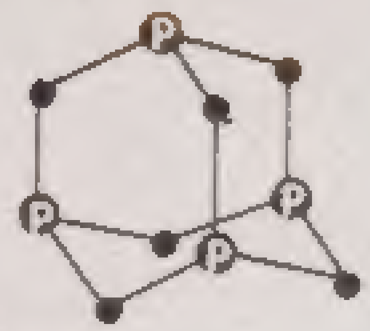
(II) Phosphorus(V) oxide, P_4O_{10}



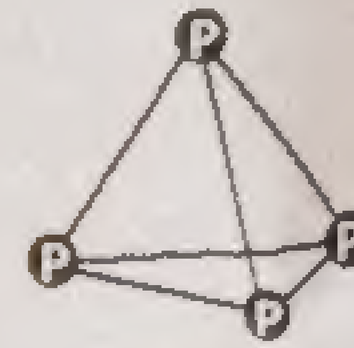
a P_4 molecu...

(I) PHOSPHORUS(III) OXIDE (P_4O_6)

- It is a white solid
- Its melting point is 24°C
- Its boiling point is 173°C.
- The structure of P_4O_6 can be obtained starting from a P_4 molecule which is a little tetrahedron.
  - ✓ Pull P_4 structure apart to see the bonds
  - ✓ Then link all the phosphorus atoms via oxygen atoms. These will be in a V-shape structure (like in water).
- The phosphorus is using only three of its outer electrons (the unpaired p electrons) to form bonds with the oxygens.



a P_4O_6 molecule

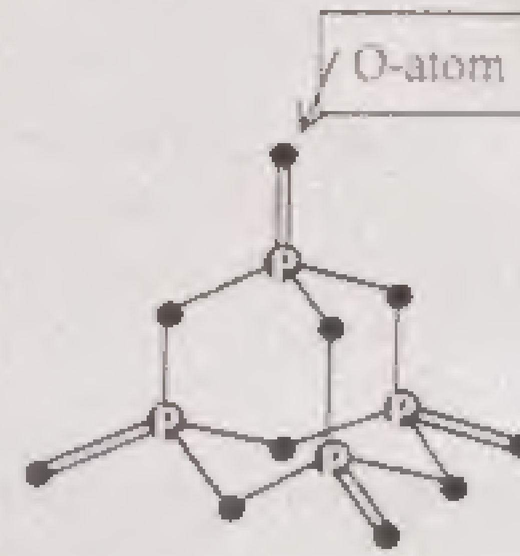


a P_4 molecule

3

(II) PHOSPHORUS(V) OXIDE (P_4O_{10})

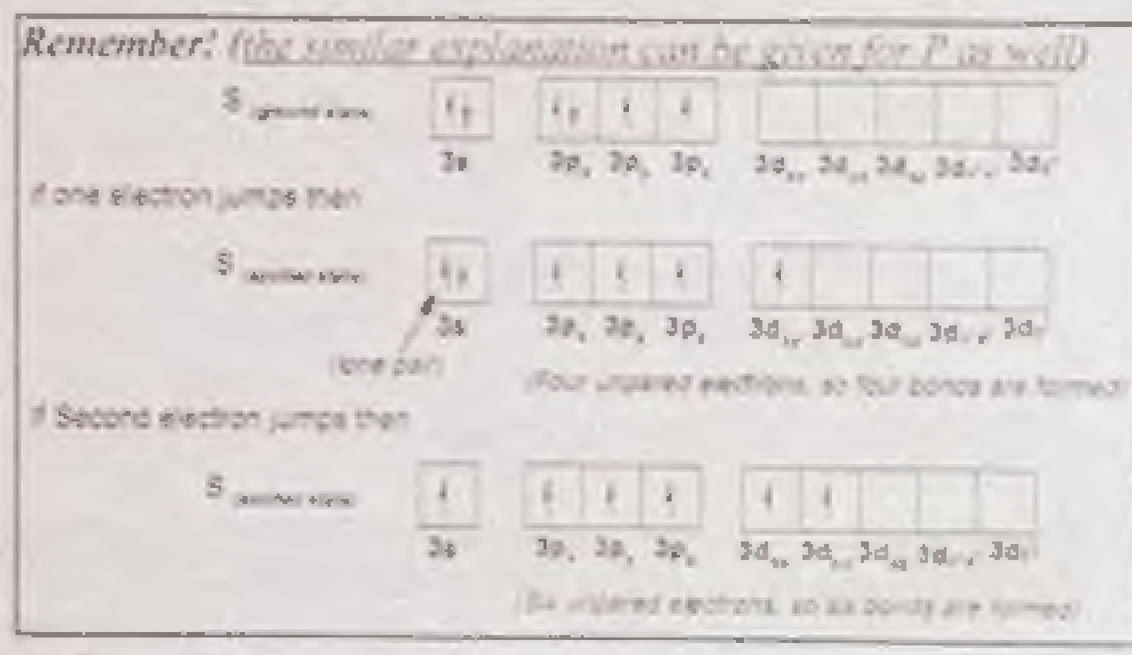
- It is a white solid
- It sublimes (turning straight from solid to vapour) at 300°C.
- Solid phosphorus(V) oxide exists in several different forms. Some of these are polymeric. The most common is the simple molecular form. This is also present in the vapour.
- In this oxide, the phosphorus uses all five of its outer electrons in the bonding.
- This is most easily drawn starting from P_4O_6. The other four oxygens are attached to the four phosphorus atoms via double bonds.



a P_4O_{10} molecule

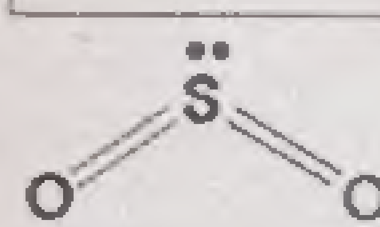
) THE SULPHUR OXIDES

Sulphur has two common oxides
(I) Sulphur dioxide (sulphur(IV) oxide), SO_2.
(II) Sulphur trioxide (sulphur(VI) oxide), SO_3.



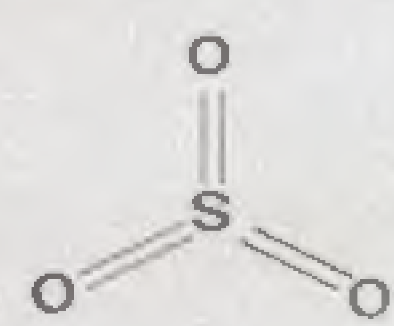
(I) SULPHUR DIOXIDE (SO_2)

- It is a colourless gas at room temperature.
- It has choking smell which can be recognised easily.
- It consists of simple SO_2 molecules.
- The sulphur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the sulphur.
- The bent shape of SO_2 is due to this lone pair.

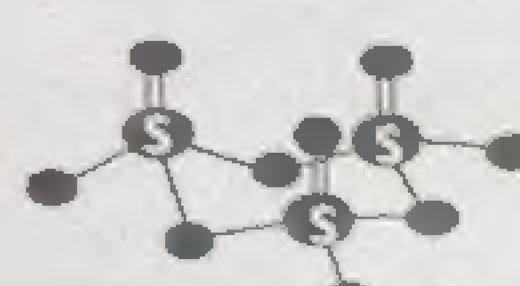


(II) SULPHUR TRIOXIDE (SO_3)

- It is a white solid
- It has low melting and boiling point.
- Gaseous sulphur trioxide consists of simple SO_3 molecules in which all six of the sulphur's outer electrons are involved in the bonding.



- There are various forms of solid sulphur trioxide. The simplest one is a trimer, S_3O_9, where three SO_3 molecules are joined up and arranged in a ring.



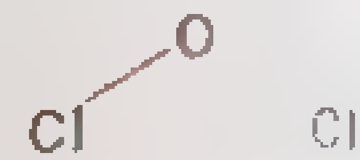
- There are also other polymeric forms in which the SO_3 molecules join together in long chains. So, the simple molecules join up in this way to make bigger structures. Thus, it makes the sulphur trioxide a solid rather than a gas.

(C) THE CHLORINE OXIDES

Chlorine forms several oxides. Two are important

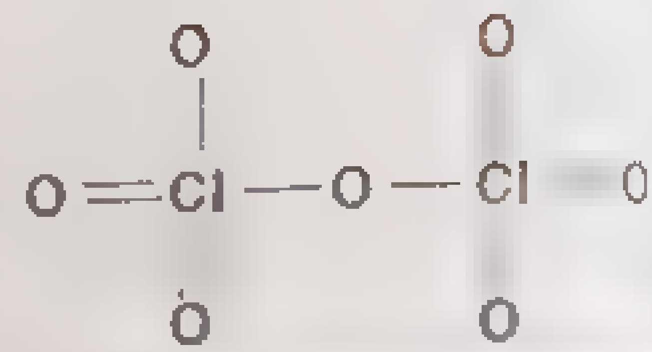
(i) Chlorine(I) oxide, Cl_2O,
(ii) Chlorine(VII) oxide, Cl_2O_7

(i) CHLORINE(I) OXIDE (Cl_2O)



- It is a yellowish-red gas at room temperature
- It consists of simple small molecules
- In this structure chlorine uses its one outer electron and bonds with oxygen

(ii) CHLORINE(VII) OXIDE (Cl_2O_7)



- It is a colourless oily liquid at room temperature
- In chlorine VII oxide the chlorine uses all of its seven outer electrons and bonds with oxygen. This produces a much bigger molecule

(ii) MELTING AND BOILING POINTS

- ***The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points,*** because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions
- The oxides of phosphorus, sulphur and chlorine consist of individual molecules. Some are small and some others polymeric
- The attractive forces between these molecules will be van der Waals dispersion and dipole-dipole interactions. These vary depending on the size, shape and polarity of the various molecules. However these forces are always much weaker than the ionic or covalent bonds of a giant structure. Thus, these oxides tend to be gases, liquids or low melting point solids

(iii) ELECTRICAL CONDUCTIVITY

- None of these oxides has any free or mobile electrons. Thus, none of them will conduct electricity when they are solid
- ***The ionic oxides can conduct electricity in molten state.*** It is because the ions become free in molten state. So, the movement of the ions towards the electrodes casuses electrical conductivity. Thus they undergo **electrolysis** when they are molten

(iv) ACID-BASE BEHAVIOUR OF THE OXIDES

The reactions of the oxides of Period 3 elements (sodium to chlorine) with water and with acids or bases show their acid-base behaviour

(A) TREND IN ACID-BASE BEHAVIOUR

A brief summary is given below

- Generally, basicity of oxides decreases and acidity increases from left to right
- The increasing acidic order from left to right is shown in Period 3 oxides

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_2	Cl_2O_7
Strongly Basic	Basic	Amphoteric	Weakly Acidic	Acidic	Strongly Acidic	Very strongly acidic

- An amphoteric oxide is one which shows both acidic and basic properties.

REACTIONS OF OXIDES WITH WATER, ACIDS AND BASES: CHEMISTRY OF THE INDIVIDUAL OXIDES

SODIUM OXIDE (Na_2O)

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion O^{2-} which is a very strong base with a high tendency to combine with hydrogen ions.

Reaction with water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.

$$Na_2O + H_2O \rightarrow 2NaOH$$

Reaction with acids

As a strong base, sodium oxide also reacts with acids, **e.g.** it would react with dilute hydrochloric acid to produce sodium chloride solution.

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

MAGNESIUM OXIDE (MgO)

- Magnesium oxide is a simple basic oxide, because it also contains oxide ions.
- However, it is less basic than sodium oxide because the oxide ions are not much free.
- In the sodium oxide case, the solid is held together by attractions between 1+ Na^+ and 2- O^{2-} ions. In the magnesium oxide case, the attractions are between 2+ Mg^{2+} and 2- O^{2-}. Thus it takes more energy to break these. So, it is a relatively a weaker base.

Reaction with water

- If some white magnesium oxide powder is shaken with water, apparently no reaction occurs.
- However, the pH of the liquid goes around pH 9 showing that solution has become slightly alkaline.
- It shows that there must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction. Since $Mg(OH)_2$ is almost insoluble in water, therefore only some hydroxide ions actually go into the solution and it becomes slightly alkaline.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Reaction with acids

Magnesium oxide reacts with acids to produce salts.

e.g. It reacts with warm dilute hydrochloric acid to give magnesium chloride solution.

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

ALUMINIUM OXIDE (Al_2O_3)

It is an amphoteric oxide. It gives reactions as both a base and an acid.

Reaction with water

Aluminium oxide does not react in a simple way with water and does not dissolve in it. Although it contains oxide ions, they are held too strongly in the solid lattice to react with the water.

Reaction with acids

Aluminium oxide reacts with hot dilute hydrochloric acid to give aluminium chloride solution.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

Reaction with bases

- Aluminium oxide also shows acidic nature, as reacts with bases such as sodium hydroxide solution.
- By this reaction various aluminates are formed. Aluminates are compounds where the aluminium is found in the negative ion. This is possible because aluminium has the ability to form covalent bonds with oxygen.
- With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

(B) REACTIONS OF OXIDES WITH WATER, ACIDS AND BASES: CHEMISTRY OF THE INDIVIDUAL OXIDES

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Reaction with acids

Aluminium oxide reacts with hot dilute hydrochloric acid to give aluminium chloride [illegible]

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

Reaction with bases

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- By this reaction various aluminates are formed. Aluminates are compounds [illegible] is found in the negative ion. This is possible because aluminium has the ability to form [illegible]
- With hot, concentrated sodium hydroxide solution, aluminium oxide reacts [illegible] sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

PHOSPHORUS(V) OXIDE (P_4O_{10})

Reaction with Water

Phosphorus(V) oxide reacts violently with water to give a solution containing a mixture of acids the nature of which depends on the conditions. Consider one of these acid, H_3PO_4 (also known just as phosphoric acid or as orthophosphoric acid)

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Reaction with Base:

Since H_3PO_4 is acidic so it reacts with NaOH solution as follows

$$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$$
$$2NaOH + H_3PO_4 \rightarrow Na_2HPO_4 + 2H_2O$$
$$3NaOH + H_3PO_4 \rightarrow Na_3PO_4 + 3H_2O$$

If phosphorus(V) oxide is reacted directly with sodium hydroxide solution then same possible salts are obtained

e.g.,

$$12NaOH + P_4O_{10} \rightarrow 4Na_3PO_4 + 6H_2O$$

Remember

$P_4O_{10} + 6H_2O \rightarrow$

$12NaOH + 4H_3PO_4 \rightarrow$

Thus adding these

$12NaOH + P_4O_{10} \rightarrow 4Na_3PO_4$

THE SULPHUR OXIDES (SO_x)

Two oxides are more important sulphur dioxide, SO_2, and sulphur trioxide SO_3

SULPHUR DIOXIDE

Reaction with Water:

Sulphur dioxide is fairly soluble in water, reacting with it to give a solution of sulphurous acid H_2SO_3

$$SO_2 + H_2O \rightarrow H_2SO_3$$

Reaction with Base:

Since it is acidic so it reacts with NaOH and CaO to produce salts

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$
$$CaO + SO_2 \rightarrow CaSO_3$$

SULPHUR TRIOXIDE

- Sulphur trioxide reacts violently with water to produce a fog of concentrated sulphuric acid droplets

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Reaction with Base:

- SO_3 reacts with NaOH aqueous solution to give Na_2SO_4

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

- In principle, sodium hydrogensulphate ($NaHSO_4$) can be obtained by using half mole sodium hydroxide that only one acidic hydrogen of H_2SO_4 is used
- Sulphur trioxide itself will also react directly with bases to form sulphates **e.g.** it will react with calcium oxide to form calcium sulphate

$$CaO + SO_3 \rightarrow CaSO_4$$

THE CHLORINE OXIDES (Cl_xO_y)

- Chlorine forms several oxides, but two are more important, chlorine(VII) oxide, Cl_2O_7, and chlorine(I) oxide Cl_2O
- Chlorine(VII) oxide is also known as dichlorine heptoxide, and chlorine(I) oxide as dichlorine monoxide

CHLORINE(VII) OXIDE

- Chlorine (VII) oxide is the highest oxide of chlorine. It means that the chlorine is in its maximum oxidation state of +7
- It has same trend of the highest oxides of the Period 3 elements. Thus it shows to be a very strongly acidic

Reaction with Water:

- Chlorine (VII) oxide reacts with water to give the very strong acid chloric (VII) acid. It is also known as perchloric acid.
- The pH of typical solutions will be around 0 just like sulphuric acid

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$

Reaction with Base:

- Chloric (VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate (VII)

$$NaOH + HClO_4 \rightarrow NaClO_4 + H_2O$$

- Chlorine(VII) oxide itself also reacts with sodium hydroxide solution to give the same product

$$2NaOH + Cl_2O_7 \rightarrow 2NaClO_4 + H_2O$$

CHLORINE(I) OXIDE

Reaction with Base:

- Chlorine(I) oxide is far less acidic than chlorine(VII) oxide
- It reacts with water to some extent to give chloric(I) acid HOCl. It is also known as hypochlorous acid

$$Cl_2O + H_2O \rightleftharpoons 2HOCl$$

Reaction with Base:

- Chloric(I) acid reacts with sodium hydroxide solution to give a solution of sodium chlorate(I) (sodium hypochlorite).

$$NaOH + HOCl \rightarrow NaOCl + H_2O$$

- Chlorine(I) oxide also reacts directly with sodium hydroxide to give the same product

$$2NaOH + Cl_2O \rightarrow 2NaOCl + H_2O$$

QUICK QUIZ-3

(a) What is the nature of bonds in the oxides formed when Na, Mg, Al and S react with excess oxygen?

Na, Mg and Al form ionic oxides. Therefore, they exists as ionic crystal line structure

S forms SO_2 and SO_3 with oxygen. These oxides have covalent bonding in them

(b) How do these oxides react with

(i) Water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution

$$Na_2O + H_2O \rightarrow 2NaOH$$

Magnesium oxide reacts with water slowly to produce alkaline solution

$$MgO + H_2O \rightarrow Mg(OH)_2$$

Aluminium oxide does not react with water. It is due to the protective coating on it which prevent it from reaction Or the reaction may be very very slow

Sulphur dioxide and sulphur trioxide reacts with water to produce H_2SO_3 and H_2SO_4 respectively

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

(ii) Dilute acids

Sodium oxide is a strong base. So, it reacts with acids to form salts

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

Magnesium oxide is basic in nature. So it reacts with acids to form salts

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

Aluminium oxide is amphoteric in nature. So, it reacts with acids to form salts

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

(iii) Alkali

Aluminium oxide is amphoteric in nature. So, it reacts with alkali to form salt

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

Since SO_2 is acidic so it reacts with alkali to produce salts

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$$

Since SO_3 is acidic so it reacts with alkali to produce salts

$$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

(c) *Magnesium chloride is a high melting point solid, aluminium chloride is a solid which sublimes readily at about 180° C and silicon tetrachloride is a volatile liquid. Explain the nature of the chemical bonding in these chlorides and show how this accounts for the above differences in volatility.*

- Magnesium chloride is an ionic solid in which ions are held together by strong ionic forces. [illegible] energy is needed to break these strong forces. Thus, it has high melting point.
- At room temperature, solid aluminium chloride has an ionic lattice with a lot of covalent [illegible] temperatures around 180 – 190°C, aluminium chloride converts to a molecular form, Al_2Cl_6 [illegible] weak intermolecular forces. Hence, it melts or sublime easily.
- Silicon tetrachloride is a simple covalent chloride. The electronegativity difference between [illegible] the chlorine is very small to form ionic bonds. Thus, the only attractions between the [illegible] Waals dispersion forces. So, it is a volatile liquid.

Important! ***(Important Concept, Not in Syllabus)***

Solubility of Salts in Water

The solubility of salts in water is mostly controlled by two factors

(i) Lattice Energy:

Briefly, it is the amount of energy required to break the crystal lattice of a salt.

- Generally, higher the lattice energy, lower the solubility and vice versa.
- Small size ions show tight packing, therefore their salts possess high lattice energies and as a result have [illegible] solubilities.

(ii) Hydration Energy:

Briefly, it is the amount of energy released when one mole of an ion dissolves in water to form infinite dilute solution.

- Generally, higher the hydration energy of ions of a salt, higher the solubility of salt.
- Small size ions dissolve easily in water, therefore, they possess high hydration energies and as a result [illegible] salts have high solubilities.

These two factors work opposite to each othere, therefore,

- In one condition, lattice energy overcomes hydration energy and thus controls the solubility **e.g.** in case of hydroxides of alkaline earth metals.
- In other condition, hydration energy overcomes lattice energy and thus controls the solubility **e.g.** in case of sulphates of alkaline earth metals.

(E) CHLORIDES OF THE PERIOD 3 ELEMENTS

(i) THE STRUCTURES

- Sodium chloride and magnesium chloride are ionic. These [illegible] temperature
- Aluminium chloride and phosp[illegible] covalent when the solid turns to a liquid or vapour
- The others are simple covalent mo[illegible]

(ii) MELTING AND BOILING POINTS

- Sodium and magnesium chlo[illegible] strong ionic attractions and a large am[illegible]
- The rest are liquids or low melting [illegible]osphorus(V) chloride
- In these the situation is quite [illegible] molecular forces such as van der Waals [illegible]
- These vary depending on the size and [illegible]ecule, but will always be far weaker than ionic bonds

(iii) ELECTRICAL CONDUCTIVITY

- Sodium and magnesium chlorides are ionic and so will underg[o] ***electrolysis*** [illegible]
- Electricity is carried by the movement of the ions and [illegible]
- In the aluminium chloride and phosphorus(V) chloride cases [illegible] the ions are not free to move. In the liquid (where it ex[illegible] they have converted into a covalent form, and so don't [illegible]
- The rest of the chlorides don't conduct electricity either [illegible] any mobile electrons

(iv) REACTIONS WITH WATER

- Sodium and magnesium chloride just dissolve in water
- The other chlorides all react with water in different ways
- The reaction with water is known as ***hydrolysis***

THE INDIVIDUAL CHLORIDES

SODIUM CHLORIDE, NaCl

- Sodium chloride is a simple ionic compoun[d] [illegible] sodium and chloride ions as shown in the figure
- The strong attractions between the positive and ne[gative] [illegible] heat energy to break. Thus, sodium chloride [illegible] points.
- It does not conduct electricity in the solid state be[cause] [illegible] mobile electrons and the ions are not free to move
- However, when it melts it undergoes electrolysis
- Sodium chloride simply dissolves in water to give a neutra[l] [illegible]

MAGNESIUM CHLORIDE, $MgCl_2$

- Magnesium chloride is also ionic, but with a more complicated arrangement of the ions to allow for having twice as many chloride ions as magnesium ions
- Again, lots of heat energy is needed to overcome the attractions between the [illegible] boiling points are again high.
- Solid magnesium chloride is a non-conductor of electricity because the ions are [illegible]
- However, it undergoes electrolysis when the ions become free on melting

- Magnesium chloride dissolves in water to give a faintly acidic solution (pH ...
- When magnesium ions are broken off the ... there are ... between the 2+ ions and the water molecules to ... the magnesium ions and lone pairs on surrounding water molecules.
- Hexaaquamagnesium ions are formed, $[Mg(H_2O)_6]^{2+}$

$$MgCl_{2(s)} + 6H_2O_{(l)} \rightarrow [Mg(H_2O)_6]^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$$

- Ions of this sort are acidic

ALUMINIUM CHLORIDE, $AlCl_3$

- At room temperature, solid aluminium chloride has ...
- At temperatures around 180 – 190°C (depending on the pressure) ... molecular form, Al_2Cl_6. This causes it to melt or vaporise ... intermolecular attractions

$$Al_2Cl_6 \rightleftharpoons 2AlCl_3$$

- As the temperature increases a bit more, it increasingly breaks up ...
- *Solid aluminium chloride does not conduct electricity at room temperature* ... to move. Molten aluminium chloride (only possible at increased ...) because still there are no ions.
- The reaction of aluminium chloride with water is surprising ... chloride, you get a violent reaction producing clouds of steamy fumes ...
- The aluminium chloride reacts with the water rather than just dissolving ... hexaaquaaluminium ions are formed together with chloride ions

$$AlCl_{3(s)} + 6H_2O_{(l)} \rightarrow [Al(H_2O)_6]^{3+}{}_{(aq)} + 3Cl^-{}_{(aq)}$$

This is very similar to the magnesium chloride equation. The ...

SILICON TETRACHLORIDE, $SiCl_4$

- Silicon tetrachloride is a simple covalent chloride. There is not enough ... the silicon and the chlorine to form ionic bonds
- Silicon tetrachloride is a colourless liquid at room temperature which fumes ... between the molecules are van der Waals dispersion forces
- It does not conduct electricity because of the lack of ions or mobile electrons.
- It fumes in moist air because it reacts with water in the air to produce hydrogen chloride.
  - ✓ If water is added to silicon tetrachloride, there is a violent reaction ... fumes of hydrogen chloride
  - ✓ In a large excess of water, the silicon tetrachloride will dissolve to give ... containing hydrochloric acid

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

THE PHOSPHORUS CHLORIDES

There are two phosphorus chlorides - phosphorus(III) chloride, PCl_3, and phosphorus(V) chloride ...

PHOSPHORUS(III) CHLORIDE (PHOSPHORUS TRICHLORIDE), PCl_3

- This is a simple covalent chloride
- It becomes a fuming liquid at room temperature
- Phosphorus trichloride is a liquid because there are only van der Waals dispersion forces ... attractions between the molecules
- It does not conduct electricity because of the lack of ions or mobile electrons.

- Phosphorus III chloride reacts ... de. If loss of water is used then a so...

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

PHOSPHORUS(V) CHLORIDE, PHOSPHORUS PENTACHLORIDE, PCl5

- Unfortunately, ph...
- Phosphorus V ...
- The higher the temperature ...

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

- Solid phosphorus ... the ions in ...
- Phosphorus(V) chloride has a ... other covalent chlorides if there is ... hydrochloric acid.
- The reaction ... along with HCl

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

- If the water is boiling, the phosphorus ... Phosphoric(V) acid is also known ... as phosphoric acid ...

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

- The overall equation in boiling water is just a combination ...

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

DISULPHUR DICHLORIDE, S2Cl2

- Disulphur dichloride is formed when chlorine reacts ...
- Disulphur dichloride is a simple covalent liquid, orange and smelly.
- The shape is difficult to draw convincingly. The atoms are ... joined up in a line but twisted.
- The reason for drawing the shape is to give a ... sort of intermolecular attractions are possible ... of symmetry in the molecule and that means ... overall permanent dipole.
- Disulphur Dichloride has van der Waals dispersion ... dipole-dipole attractions.
- There are no ions in disulphur dichloride and ...
- Disulphur dichloride reacts slowly with water to produce a ... acid, sulphur, hydrogen sulphide and various ...

QUICK QUIZ-4

1. *Which of the following give acidic solution in water: $MgCl_2$, $AlCl_3$, $SiCl_4$, $NaCl$*

- $MgCl_2$ and NaCl are salts of strong acids and strong bases. So they ... neutral.
- In a large excess of water, $SiCl_4$ will dissolve to give a strongly acidic ...

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

- $AlCl_3$ is a salt of strong acid and weak base. It reacts with water ...

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

Salt + water   Base   Acid

2. ***Why NaCl has high melting and boiling point***
Sodium chloride is an ionic solid in which ions are held together by strong ion ... needed to break these strong forces. Thus, it has high melting and boiling points.

3. ***Write equations for reactions of PCl_5 with hot and cold water.***
The reaction occurs in two stages
In the first, with cold water phosphorus oxychloride $POCl_3$, is produced along with HC...

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$$

If the water is boiling, the phosphorus(V) chloride reacts further to give phosphoric(V ...

$$POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

Add the above two reactions to get the overall equation

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

4. ***What products are obtained on reaction of disulphide dichloride with water.***
Disulphur dichloride reacts slowly with water to produce a complex mixture of ... acid, sulphur, hydrogen sulphide and various sulphur containing acids and anions

$$2\,S_2Cl_2 + 2\,H_2O \rightarrow SO_2 + 4\,HCl + \frac{3}{8}S_8$$

and $S_2Cl_2 + 2H_2O \rightarrow H_2S + SO_2 + 2HCl$ etc.

5. ***Why $AlCl_3$ is non-conductor in solid as well as in liquid state but NaCl and $MgCl_2$ are conductor in ... state and non-conductor in solid state.***

- NaCl and $MgCl_2$ do not conduct electricity in the solid state. It is because they do not have a... the ions free to move. However, they undergo electrolysis when the ions become free on melting.
- Solid aluminium chloride does not conduct electricity at room temperature because the ... move. Molten aluminium chloride also does not conduct electricity because still there are no free ...

HYDROXIDES OF THE PERIOD 3 ELEMENTS

SODIUM AND MAGNESIUM HYDROXIDES

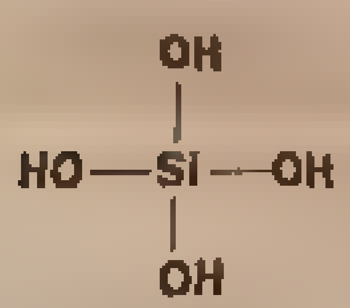
- These contain hydroxide ions, and are simple basic hydroxides

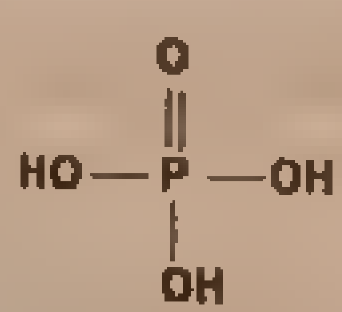
ALUMINIUM HYDROXIDE

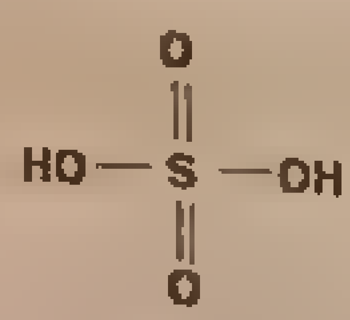
- Aluminium hydroxide, like aluminium oxide, is amphoteric. Thus, it has both basic and acidic ...

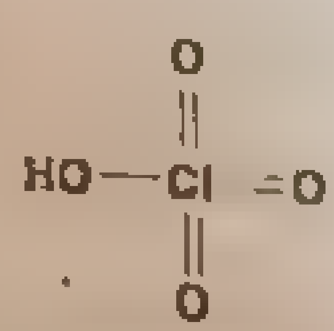
THE OTHER "HYDROXIDES"

- In all of these have -OH groups covalently bound to the atom from period 3
- These compounds are all acidic. These range from the very weakly acidic silicic acids to the ... sulphuric or chloric acids.
- There are other acids (also containing -OH groups) formed by these elements, but these are ... where the Period 3 element is in its highest oxidation state


orthosilicic acid


phosphoric(V) acid


sulphuric acid


chloric(VII) acid

SODIUM AND MAGNESIUM HYDROXIDES

- These ...
- Both ... e g

$NaOH + HCl \rightarrow NaCl + H_2O$

$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

ALUMINIUM HYDROXIDE

- Aluminium hydroxide ...
- Like sodium ...
  With dilute ...

$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$

- But aluminium hydroxide ...
  give a ...

$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$

THE OTHER "HYDROXIDES"

- Orthosilicic acid is very weak
- Phosphoric(V) acid is a weak ...
- Sulphuric acid and ...
- The main factor in determining ... hydrogen has been removed ... rest of the ion
- If the negative charge stays entire ... to hydrogen ions. The lost hyd...
- On the other hand, if the charge ... that it won't attract the hydrogen ...

QUICK QUIZ-5

1. ***Which factor determines the strength of acid***

Two factors are responsible for the strength of ...

(i) Ease of donation of proton. Bond Energy

Greater the ease of donation of proton, hi... Thus, higher the bond energy, lesser is the ... acidity order among halogen acids is HI > ...

(ii) Stability of the anion (conjugate base)

Greater the stability of anion, higher is the acidity. A ... anion by attracting electrons of anion towards itself e.g.

$$HClO_4 \rightleftharpoons H^+ + ClO_4^{-1}$$

In this the anion $(ClO_4)^{-1}$ is stabilized by ... are highly electronegative elements. Thus, $HClO_4$ is the ...

2. ***Justify that $Al(OH)_3$ is amphoteric compound.***

$Al(OH)_3$ reacts with both acids and bases to form ...

Reaction with acid	$Al(OH)_3 + 3HCl$	$\rightarrow$	$AlCl_3 + 3H_2O$
Reaction with base	$Al(OH)_3 + NaOH$	$\rightarrow$	$NaAl(OH)_4$

ATOMIC AND PHYSICAL PROPERTIES OF THE GROUP 1 ELEMENTS

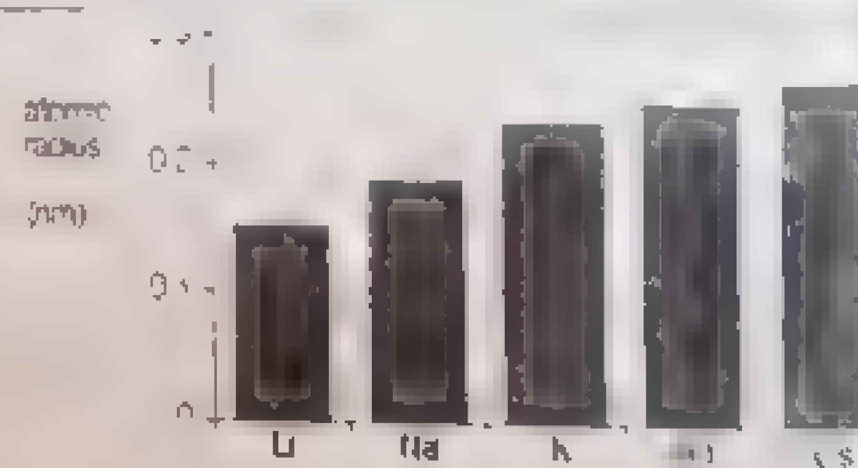
Table: Some Physical Properties of alkali metals

Property	Li	Na	K	Rb	Cs
Atomic weight	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Atomic volume	12.97	[illegible]	[illegible]	[illegible]	[illegible]
Atomic (metallic radius for coordination number 12)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
covalent radius	1.23	[illegible]	[illegible]	[illegible]	[illegible]
Ionic radius of M+ ions	0.6	[illegible]	[illegible]	[illegible]	[illegible]
Melting point	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Boiling point	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Ionization energies (kJ/mol) (I_1)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
I_2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Standard oxidation potential	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Sublimation energy (eV/ion)	1.7472	[illegible]	[illegible]	[illegible]	[illegible]
Hydration energy (eV/ion)	5.904	[illegible]	[illegible]	[illegible]	[illegible]
Electronegativity	1	[illegible]	[illegible]	[illegible]	[illegible]
Colour of the flame	Crimson red	[illegible]	[illegible]	[illegible]	[illegible]
Heat of atomisation at 25C (eV/atm)	1.7472	[illegible]	[illegible]	[illegible]	[illegible]
Ionic conduction of M+ ion	33.5	[illegible]	[illegible]	[illegible]	[illegible]

Shielding Effect or Screening Effect: *The decrease in attraction between [illegible] inner shells electrons is called Shieding effect or screening effect*

TRENDS IN ATOMIC RADIUS

The distance of outermost electron from the nucleus of an atom while considering it spherical is called atomic radius.



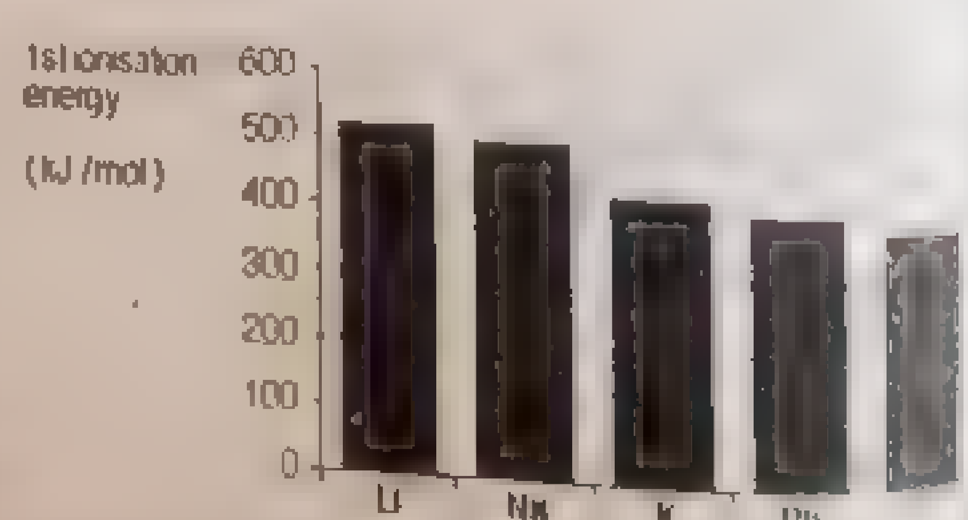
The atomic radius increases down the group from lithium to caesium. It is because, down the group number of shells increases. So, the atomic volume increases. Moreover, the shielding effect of inner electrons also increases. Hence, atomic and ionic radii (of M^+ ions) increases from lithium to caesium

TRENDS IN FIRST IONIZATION ENERGY

First ionization energy is the energy needed to remove the most loosely held electron [illegible] gaseous atoms to make one mole of singly charged gaseous ions

$$M_{(g)} \rightarrow M^+_{(g)} + e^-$$

The first ionization energy decreases down the group.

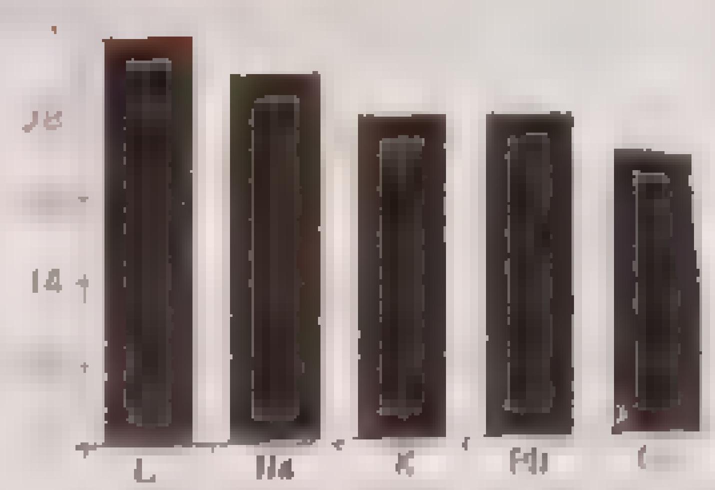


- The alkali metals have only one electron in their outermost shell (ns1 electron). This ns^1 electron is weakly held with the nucleus. Thus, it can be removed very easily Therefore, Alkali metals have low ionization energies.
- The distance of ns^1 electron from the nucleus increases from Li to Cs due to increase in atomic size Thus its removal becomes more and more easy and the amount of energy required for the removal of ns^1 electron also decreases. Hence, ionisat[illegible] alkali metals decrease from Li to Cs.
- The second ionization energies are fairly high, since the loss of the second electron from M^+ ion has a noble gas configuration [illegible]

TRENDS IN ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons

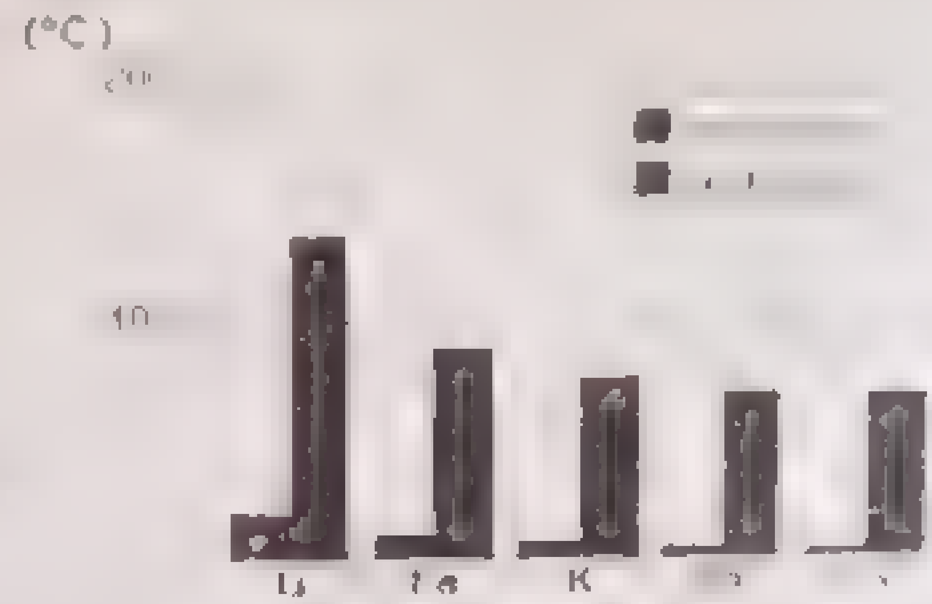
- It is usually measured on the Pauling scale on which the most electronegative element fluorine is given an electronegativity of 4.0
- It has no unit.
- The electronegativity values decreases down the group from Li to Cs due to increase in atomic size



TRENDS IN MELTING AND BOILING POINTS

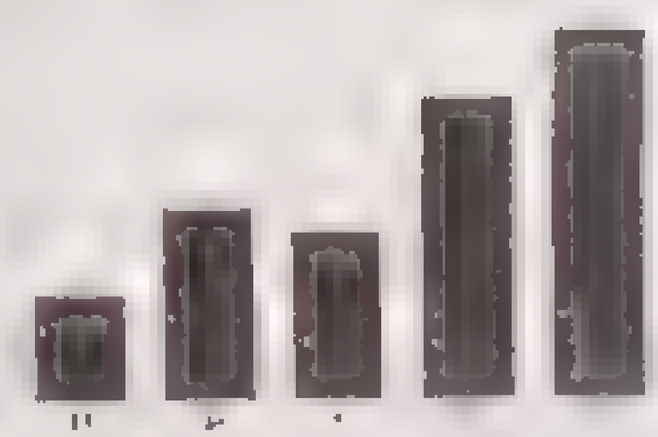
Both the melting points and boiling points decrease down the Group.

- The melting and boiling points are very low due to the presence of weak inter-atomic bonds in the solid state of the alkali metals
- The bonds are weak due to their larger atomic radii and mainly due to a single valence electron as compared to large number of available vacant orbital
- As the size of the metal atoms increases, the repulsion of the non-bonding electrons also increases. This increase in the repulsion of non-bonding electron decreases the melting and boiling points of alkali metals from Li to Cs



TRENDS IN DENSITY

- The densities of alkali metals are quite low due to ... atomic volumes as shown in the figure
- Li, Na and K are lighter than water
- The densities increase with the increase in at... Li to Cs. It is because increase in atomic mass is ... the increase in atomic volume So, the density incr...
- K is however, lighter than Na. It is due to an unusu... in atomic volume of K



Elements	Li	Na	K	Rb	Cs
Densities at 0°C (g/c.c)	0.534	0.972	0.859	[illegible]	[illegible]

QUICK QUIZ-6

1. ***Different element imparts different colours in flame?***

   In certain metals the outer electron is loosely held ... energy levels even by absorbing a small amount of ene... its original position, it gives out absorbed energy in the ... coloured The amount of energy absorbed during the excitati... different colours are imparted by the atoms to the flame

2. ***Explain that 2^{nd} ionization energy is greater than 1^{st} ionization energy***

   It is because, due to removal of first electron hold ... second electron is difficult to remove and thus ionization e...

   Examples:

   $Mg_{(g)} \rightarrow Mg_{(g)}^{+} + e^-$ $\Delta H = +738$ kJ/mole

   $Mg_{(g)}^{+} \rightarrow Mg_{(g)}^{2+} + e^-$ $\Delta H = +1451$ kJ/mole

3. Why melting point of alkali metals are low as compared to alkaline earth metals

It is due to two reasons

- The atomic radii of alkaline earth metals are smaller than those of alkali metals in the same period. Alkaline earth metals have relatively tight packing of atoms. So they are harder and have higher [illegible] than alkali metals.
- Alkali metals have one valence electron. Thus they provide one electron per atom for binding. Alkaline earth metals provide two electrons per atom for binding. So they have stronger binding forces and higher melting points than alkali metals.

CHEMICAL PROPERTIES OF THE GROUP 1 ELEMENTS

REACTIONS WITH WATER

- With the exception of Li, the alkali metals are extremely soft and readily fused.
- They are highly malleable (i.e. can be pressed out into sheets) and ductile (i.e. can be drawn into [illegible]).
- When freshly cut, they have a bright lustre.
- They are quickly tarnished as soon as metal comes in contact with atmosphere.
- The reactivity of Group 1 metals increases down the Group.

Enthalpy changes for the reactions

- Generally, enthalpy of reaction increases from Li to Cs.

  $$M_{(s)} + H_2O_{(l)} \rightarrow MOH_{(aq)} + \frac{1}{2}H_{2(g)}$$

- However, there is no regular pattern in these values. They are all fairly similar.
- Lithium releases the most heat during the reaction.
- In each case, metal atoms in a solid form are reacted and metal ions are formed in the solution.
- Overall, what happens to the metal is this

  $$M_{(s)} \rightarrow M^{+}_{(aq)} + e^{-}$$

	Enthalpy change (kJ / mol)
Li	222
Na	-184
K	196
Rb	195
Cs	203

REACTIONS WITH OXYGEN

- Alkali metals react with O_2 or air rapidly and thus get tarnished due to the formation of their oxide on surface of the metals. That is why alkali metals are stored in kerosene or paraffin oil.
- Li when burnt in O_2 gives mainly lithium monoxide, (normal oxide) Li_2O.

  $$4Li + O_2 \rightarrow 2Li_2O$$

- Na when burnt in O_2 forms sodium peroxide, Na_2O_2

  $$2Na + O_2 \rightarrow Na_2O_2$$

- Other alkali metals react with O_2 to form super oxide of MO_2 type

  $$M + O_2 \rightarrow MO_2$$

- Normal oxides of alkali metals are not formed by the direct reaction between the metals and O_2 except (Li_2O). They are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metal itself.

  $$2Na_2O_2 + 4Na \rightarrow 4Na_2O$$
  $$2NaNO_2 + 6Na \rightarrow 4Na_2O + N_2$$
  $$2NaNO_3 + 10Na \rightarrow 6Na_2O + N_2$$

Properties.

- Normal oxides (O^{2-}) react with H_2O to form hydroxides by proton exchange

Gains proton

$$O^{2-} + H_2O \rightleftharpoons OH^- + OH^-$$

- The peroxides (O_2^{2-}) and superoxides O^{2} ... s. These react with H_2O to give H_2O_2 and O_2

$$O_2^{2-} + 2H_2O \rightarrow H_2O_2$$
$$2[O\text{-}O] + 2H_2O \rightarrow H_2O_2 + O_2$$

- Normal oxides have anti-fluorite structure. They are ionic in nature since they contain monoxide ion, O^{2-}
- Peroxides contain peroxide ion, O_2^{2-} or [O-O]$^{2-}$
- The super oxide ion has a three electron bond as shown below

$$(O - \cdot O)^-$$

- The presence of one unpaired electron in it makes this in ... coloured.

REACTIONS WITH CHLORINE

- Sodium burns with an intense orange flame in chlorine in the same way as it does in pure oxygen
- The rest also behave the same in both cases
- In each case, a white solid is produced which is the simple chloride, MCl

$$2M + Cl_2 \rightarrow 2MCl$$

CHEMICAL PROPERTIES OF THE COMPOUNDS OF GROUP 1 ELEMENTS

REACTIONS OF THE OXIDES WITH WATER AND DILUTE ACIDS

(i) THE SIMPLE OXIDES, X_2O

Reaction with water

These are simple basic oxides, reacting with water to give the metal ... e.g. ... oxide reacts with water to give a colourless solution of lithium hydroxide

$$M_2O + H_2O \rightarrow 2MOH$$

Reaction with dilute acids

These simple oxides all react with an acid to give a salt and water e.g. ... hydrochloric acid to give colourless sodium chloride solution and water

$$M_2O + 2HCl \rightarrow 2MCl + H_2O$$

(ii) THE PEROXIDES, X_2O_2

Reaction with water

- If the reaction is done ice cold then a solution of the metal hydroxide and hydr... These reactions are strongly exothermic. However, during reaction the tempe... does not rise.

$$M_2O_2 + 2H_2O \rightarrow 2MOH + H_2O_2$$

- If the temperature increases, the hydrogen peroxide produced decompose... reaction can be very violent overall
- The temperature rise is generally certain. However, it can be controlled by adding the ... to water

-
-
-

$MO + 2HCl \rightarrow 2MCl + H_2O_2$

THE SUPEROXIDES MO_2

Reaction with water

-
-

$$2MO_2 + 2H_2O \rightarrow 2MOH + H_2O_2 + O_2$$

Reaction with dilute acids

-
-
- ... peroxide will again decompose ...

$$2MO_2 + 2HCl \rightarrow 2MCl + H_2O_2 + O_2$$

EFFECT OF HEAT ON NITRATES, CARBONATES AND HYDROGEN-CARBONATES

(i) THE FACTS

Group 1 compounds are more stable to heat than the corresponding ...

The lithium compounds behave similarly to Group 2 compounds

The rest of Group 1 behave similarly but in a different way than Group 2

Nature of carbonates, bicarbonates and nitrates

- The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) are highly stable to heat
- With increase of electropositive character from Li to Cs, the stability of these salts increases
- Their nitrates decompose on strong heating to the corresponding nitrite and O_2

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

- The $LiNO_3$ decomposes completely to give corresponding oxide, NO_2 and O_2

$$3LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

QUICK QUIZ-7

(ii) EXPLAINING THE TREND IN TERMS OF THE POLARISING ABILITY OF THE POSITIVE ION

1. ***Why lithium salts are more covalent in nature while salts of other alkali metals are ionic.***

When cations approach near an anion, they attract the outer most electrons of the anion and repels the nucleus. Thus the distortion or polarization of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions. So, a bond between the cation and anion becomes partly covalent in character. *In general the smaller cations polarize the anions more effectively than bigger one. Therefore, the lithium salts are slightly covalent while other alkali metal salts are ionic*

2. ***Give trend of stability of carbonates of alkali and alkaline earth metals along group.***

- The solubility of alkali metal carbonates increases down the group due to increase in ionic character
- Generally, the solubility of alkaline earth metal carbonates decreases down the group except $BaCO_3$ which has slightly more solubility than $SrCO_3$. So, a clean trend is not found.

3. Show bonding in superoxide ion

- The super oxide ion ha...

(O O)

- The presence of one unpaired ...

4. Why alkali metals stores in kerosene or paraffin oil

Alkali metals react with ... surface of the metal. ... are stored in kerosene or par...

FLAME TESTS

- Flame tests are used to identify the ... compound
- All metal ions do not give flame ...
- Flame tests is the easiest way ...
- For other metals, there ...

PROCEDURE FOR FLAME TEST

- Take a platinum or nichrome (a nickel chromium alloy) wire
- Clean it by dipping it into concentrated hydr...
- Repeat this until the wire does not produce any ...
- Moisten the clean wire ... sticks to the wire
- Place the wire back in the flame again
- If the flame colour is weak, then dip the wire back in the acid again and put it back into the f...
- A very short but intense flash of colour is obtained
- Different colours are shown by different el...

RESULT: THE COLOURS

Different colours shown by different ...

FLAME COLOUR

How to differentiate between different red colours obtained in flame test?

- Get samples of known lithium, strontium ... compound
- Repeat the flame test with known and unknown ...
- Comparing the colour produced by known compounds and the unknown compound side by side until a good match ...

THE ORIGIN OF FLAME COLOURS

- In alkali metal atoms the outer ns^1 electron is loosely held which ... the higher energy levels even by a small amount of heat ... Bunsen bur...

- The ...
- The prop... in salts. This test is known a...

QUICK QUIZ-8

(1) Ion of which element among the alkali metals has the greatest polarizing power?

In general, the smaller cations polarize the ... has the greatest polarizing power

(2) Justify the placing of Li, Na, K, Rb, and Cs in the same group of the periodic table

The valence shell electronic configuration of Li is $2s^1$ ... (ns^1). Thus, due to similar electronic configuration, Li shows ... alkali metals group

(3) Write the electronic configuration for alkali metal atoms.

Element	Electronic Configuration	Short configuration
Li	$1s^2\,2s^1$	
Na	$1s^2\,2s^2\,2p^6\,3s^1$	
K	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^1$	
Rb	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^1$	
Cs	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^1$	
Fr	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^{14}\,5d^{10}\,6p^6$ [illegible]	

(4) Explain the periodicity in ionization energy, electronegativity and atomic radii on passing from Li to Rb

- Atomic radii increases from Li to Rb due to increase in number of shells and shielding effect
- Ionization energy decreases from Li to Rb due to increase in size
- Electronegativity decreases from Li to Rb due to increase in size

(5) Among alkali metals atoms which has the largest ionization potential?

Lithium (Li) metal has highest ionization energy due to its smallest size among alkali metals

(6) Explain the following.

(a) Alkali metals show an oxidation state +1 only

Alkali metals have only one valence electron which is easily lost due to low first ionization energy. After loss of one electron, they get the noble gas configuration. So, it becomes highly difficult to remove second electron from them. Therefore, they have high second ionization energy. Hence they do not show oxidation state greater than +1.

(b) Alkali metals are univalent.

Alkali metals have only one valence electron which is easily lost due to low first ionization energy. After the loss of one electron, they get the noble gas configuration. So, it becomes highly difficult to remove second electron from them. Therefore, they have high second ionization energy. Hence they are univalent.

(c) alkali metals are good reducing agents

Alkali metals have low ionization energy. So, they can easily loose electrons i.e. they are easily oxidized. Thus they can reduce substances and act as excellent reducing agents.

(d) alkali metals have low m.pts

Alkali metals have only one valence electron. So, they provide only one electron for binding. Therefore they have weaker binding forces and hence they have low melting points

e) **Alkali metals give characteristic colour to the Bunsen flame**

It alkali metals ... nucleus. So it can be easily excited to the ... electron ... it gives out absorbed energy in the form of light in the visible region ...

f) **Na is stored under kerosene**

...

g) **Alkali metals form M^{+} cations instead of M^{2+} cations**

...

h) **Alkali metals ...**

... their outermost electron are loose ...

7) **Hydroxides of 1st group are strong bases. Explain why?**

Since alkali metals ... are larger in size therefore their bases have low lattice energies. So ... in water dissolve and produce high concentration of OH^{-} ions. Hence hydroxides of 1st group are strong bases.

8) **Explain the following**

Li_2CO_3 is unstable ... carbonates are ... stable.

Since ...

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

Moreover ... on heating ...

GROUP 2 ELEMENTS

ATOMIC AND PHYSICAL PROPERTIES

The Group 2 elements ...

TRENDS IN ATOMIC RADIUS

- The figure shows ...
- ... Group.
- The atomic radius increases ... because down the group ... volume increases. Hence ... increases from Be to Ra.
- The atomic radii of these elements ... alkali metals in the same period ... have higher nuclear charge ... nucleus.
- Due to smaller atomic radii the ... points than alkali metals.

The Table gives some physical properties ...

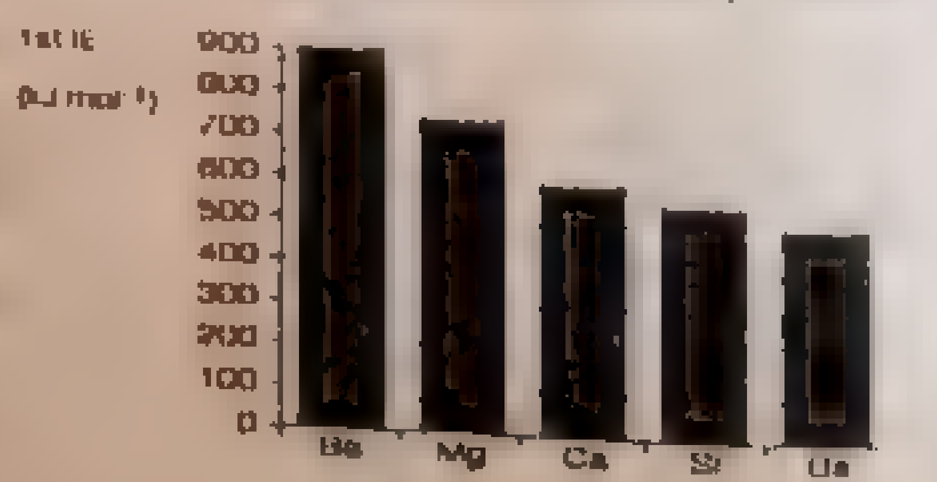
Property	Be	Mg	Ca	Sr	Ba	[illegible]
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	6.4 x 10.4	2.0	3.45	0.915	0.040	1.3x10 [illegible]
Density (gm/c.c.)	1.84	1.74	1.55	2.54	3.75	[illegible]
Melting point (°C)	1277	650	838	763	714	[illegible]
Boiling point (°C)	2770	1107	1440	1380	1640	
Atomic volume (c.c.)	4.90	13.97	25.9	34.54	36.7	38.0
Atomic (i.e., metallic) radius for co-ordination number 12 (A°)	1.12	1.60	1.97	2.15	2.22	
Covalent radius (A°)	0.90	1.36	1.74	1.91	1.98	
Ionic (crystal radius of M^{2+} ion for co-ordination number + (A°)	0.31	0.65	0.99	1.13	1.35	1.40
Ionisation energies (KJ/mole)						
I_1	899.5	737.7	829.8	547.5	502.9	509.4
I_2	1757.1	1450.7	1145.4	1064.3	965.2	[illegible]
$I_1 + I_2$	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation state	+2	+2	+2	+2	+2	+2
Electronegativity	1.5	1.2	1.0	0.9	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for M (s) $\longrightarrow$ M^{2+} (aq) + 2e	1.70 1.70	1.37	2.87	2.89	2.90	2.92
Heat of automization at 25°C and 1 atm pressure (KJ/mole)	327.26	146.89	181.21	163.21	175.[illegible]	
Heat of hydration (KJ/mole)	2385.45	1925.1	1653.07	1458.67	1276.42	
Ionic potential of M2 + ion (i.e., charge/ radius ratio)	6.66	3.08	2.12	1.82	1.55	1.43

TRENDS IN FIRST IONIZATION ENERGY

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole gaseous atoms to make one mole of singly charged gaseous ions

$$M_{(g)} \rightarrow M^{+}_{(g)} + 2e^-$$

First Ionisation Energy of the Group 2 elements



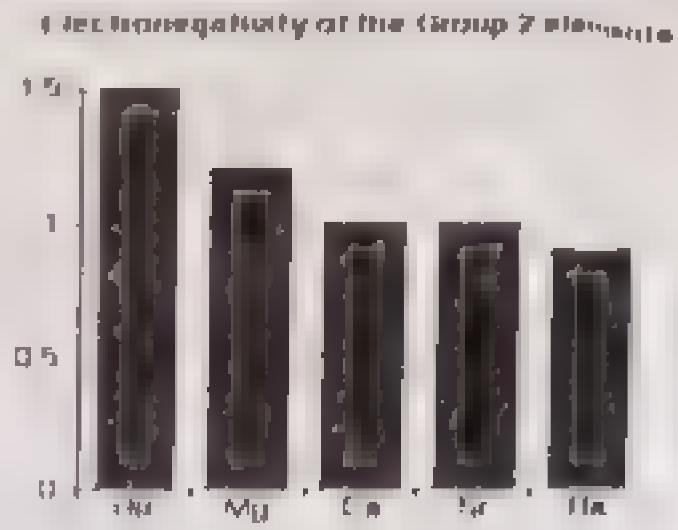
- The figure shows the first ionization energy of the Group 2 elements
- <u>**The first and second ionization energies of these elements decrease with the increase of atomic radii from Be to Ba.**</u>

  It is because the distance of outer electrons from the nucleus increases from Be to Ra due to increase in atomic size. So, removal of electrons becomes more and more easy and thus amount of energy required for the removal electrons also decreases. Hence, ionization energies decreases from Be to Ra.
- Ra has slightly higher first and second ionization energies than Ba

TRENDS IN ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

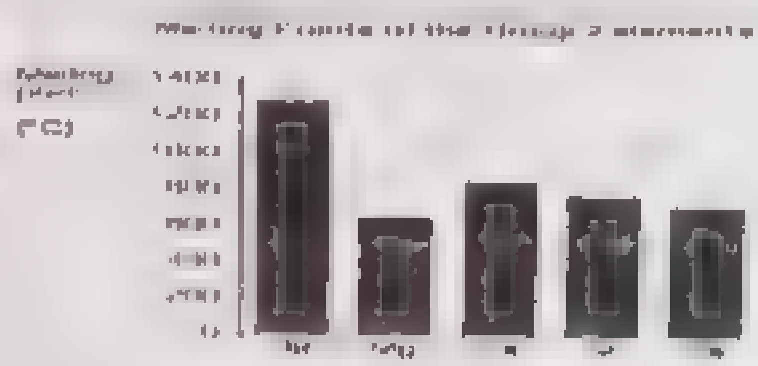
- It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0
- It has no unit
- The figure shows the electronegativities of the Group 2 elements.



- ***The electronegativity values increases down the group.***
- It is due to following reasons
  - ✓ Down the group atomic size increases. Thus, the distance of bonding pair increases from the metal nucleus. Hence, bonding pairs are less strongly attracted and so, the electronegativity decreases
  - ✓ Moreover, the bonds formed between these metals and other things (e.g. chlorine) become more and more ionic down the group. Thus, the bonding pair is pulled away from the Group 2 element towards the other things (e.g. chlorine)

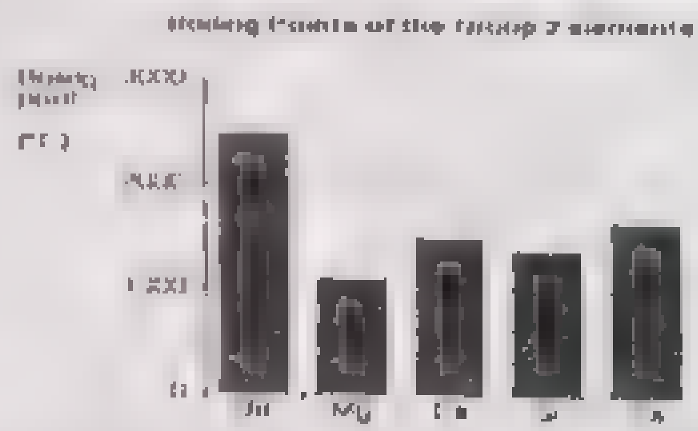
TRENDS IN MELTING POINT AND BOILING POINT

- ***The melting and boiling points of Group 2 elements are higher than Group 1 elements.*** It is because Group 2 elements have two valence electrons. So, they form greater number of bonds than Group 1 elements
- Generally, no regular trend is present in the melting and boiling points of Group 2 elements



Melting points

The figure shows that the melting point decreases down the Group. However, the smooth decreasing trend is broken by magnesium



Boiling points

The figure shows that there is no regular pattern in boiling points

CHEMICAL PROPERTIES OF THE ELEMENTS OF GROUP 2 ELEMENTS

REACTIONS WITH WATER

The reactivity increases down the group. It is because down the group ability to give electrons increases

THE FACTS

Beryllium

Beryllium has no reaction with water or steam even at red heat

Magnesium

- Magnesium burns in steam to produce white magnesium oxide and hydrogen gas

$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$

- Very clean magnesium ribbon has a very slight reaction with cold water. ... some bubbles of hydrogen form on its surface. The coil of magnesium ribbon usually ...
- However, the reaction soon stops because the magnesium hydroxide form ... in water and forms a barrier on the magnesium preventing further reaction

$$Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(s)} + H_{2(g)}$$

Calcium, Strontium and Barium

- [illegible]
- [illegible]
- [illegible]
- The equation for the reactions of any of these metals would be

$$M_{(s)} + 2H_2O_{(l)} \rightarrow M(OH)_{2(aq)} + H_{2(g)}$$

- The solubility of the hydroxides increases down the Group
- The calcium hydroxide forms mainly as a white precipitate because [illegible] However, down the group less precipitates are formed because [illegible] group
- The Group 2 metals become more reactive towards water as you go down the Group

TREND IN REACTIVITY

- $Be(OH)_2$ is not at all basic. It is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates

$$Be(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

- The hydroxides of other metals are basic in nature
- ***The basic character increases on moving down the group.*** Thus $Mg(OH)_2$ is weakest base [illegible] the strongest base. It is because with the increase in size of M^{2+} cation, both the polarity [illegible] the internuclear distance between oxygen of OH^- ion and the metals atom increase. Thus [illegible] ionization of $M(OH)_2$ and hence basic character increases
- Due to high polarising power of small Be^{2+} in $Be(OH)_2$, it is covalent. All other hydroxides are ionic
- The solubility of hydroxides increases down the Group as shown by the solubility products

$Be(OH)_2 = 1.6 \times 10^{-26}$ $Mg(OH)_2 = 8.9 \times 10^{-12}$
$Ca(OH)_2 = 1.3 \times 10^{-6}$ $Sr(OH)_2 = 3.2 \times 10^{-4}$ $Ba(OH)_2 = 5.4 \times 10^{-2}$

- Thus, $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in H_2O. The hydroxides of other metals are [illegible] soluble

REACTIONS WITH OXYGEN AND NITROGEN

(a) FORMATION OF SIMPLE OXIDES

- The alkaline earth metals form the normal oxides of MO type
- These are obtained either by heating the metal in O_2 or by heating their carbonates at high temperature

$$2Ca + O_2 \rightarrow 2CaO$$
$$CaCO_3 \rightarrow CaO + CO_2$$

Properties:

- These oxides are extremely stable white crystal line solids due to their high crystal lattice energy obtained packing doubly charged in an a sodium chloride type of lattice
- BeO and MgO are quite insoluble in H_2O while H_2O CaO, SrO qand BaO react with H_2O to give soluble hydroxides, $M(OH)_2$ which are strong bases
- BeO is not basic in nature. In fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates,

$$Be(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$
$$Be(OH)_2 + 2NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

- The oxides of other metals are basic in character. Their basic character [illegible] the group
- Be^{2+} ion has high polarizing power due to small size. Thus BeO is covalent [illegible]
- Although BeO is covalent yet is has a higher melting point and is harder than the oxides of other [illegible] and is polymeric
- Each Be atom is tetrahedrally coordinated by four oxygen atoms

(b) FORMATION OF PEROXIDES.

- The peroxides of heavier metals (Ca, Sr, Ba etc.) can be obtained on heating [illegible] high temperature

$$2BaO + O_2 \rightarrow 2BaO_2$$

Properties:

- The peroxides are white ionic solids having peroxide anion $(O-O)^{2-}$
- They react with acids to produce H_2O_2

(c) FORMATION OF NITRIDES ON HEATING IN AIR

- All the elements burn in nitrogen to form nitrides, M_3N_2 e.g.

$$3Ca + N_2 \rightarrow Ca_3N_2$$

- These react with H_2O to liberate NH_3

$$2Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 6NH_3$$

- Be_3N_2 is volatile while other nitrides are not so

TRENDS IN SOLUBILITY OF THE HYDROXIDES, SULPHATES AND CARBONATES

I- SOLUBILITY OF THE HYDROXIDES

The solubility of hydroxides of Group 2 metals increases down the Group

Magnesium hydroxide

It appears to be insoluble in water. However, shake it with water, filter it and test the pH of the solution, it will be slightly alkaline. It shows that there are more hydroxide ions in the solution than pure water. So, some magnesium hydroxide must have dissolved

Calcium hydroxide

Its solution is used as "lime water". One litre of pure water will dissolve about 1 gram of calcium hydroxide at room temperature

Barium hydroxide

It is soluble enough and produce a solution with a concentration of around 0.1 mol dm^{-3} at room temperature

II- SOLUBILITY OF THE SULPHATES

The solubility of sulphates of Group 2 metals decreases down the Group

III- SOLUBILITY OF THE CARBONATES

- The solubility of carbonates of Group 2 metals decreases down the Group
- Carbonates are insoluble in water and therefore occur as solid rock minerals in nature
- However they dissolve in H_2O containing CO_2 due to the formation of bicarbonates

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

TRENDS IN THERMAL STABILITY OF THE CARBONATES AND NITRATES

[illegible]

[illegible]

[illegible]

Summary

- [illegible]
- [illegible]

HOW BERYLLIUM DIFFER FROM OTHER MEMBERS OF ITS GROUP?

[illegible]

1. [illegible]
2. **Melting and boiling points:** [illegible]
3. **Formation of covalent compounds:** [illegible]
4. **Reaction with water:** [illegible]

   $Mg + H_2O \rightarrow MgO + H_2$

5. **Reaction with hydrogen:** [illegible]
6. **Reaction with alkalies:** Beryllium reacts with alkalis [illegible]

   $Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$

Other alkaline earth metals do not react with alkalis.

7. ***Behaviour of oxides and hydroxides:*** The oxides and hydroxides of beryllium are amphoteric i.e. dissolve in both acids and alkalis to form salts

$$BeO + H_2SO_4 \rightarrow BeSO_4 + H_2O$$

8. ***Behaviour of carbides*** Beryllium carbide is decomposed by water to form methane (CH_4)

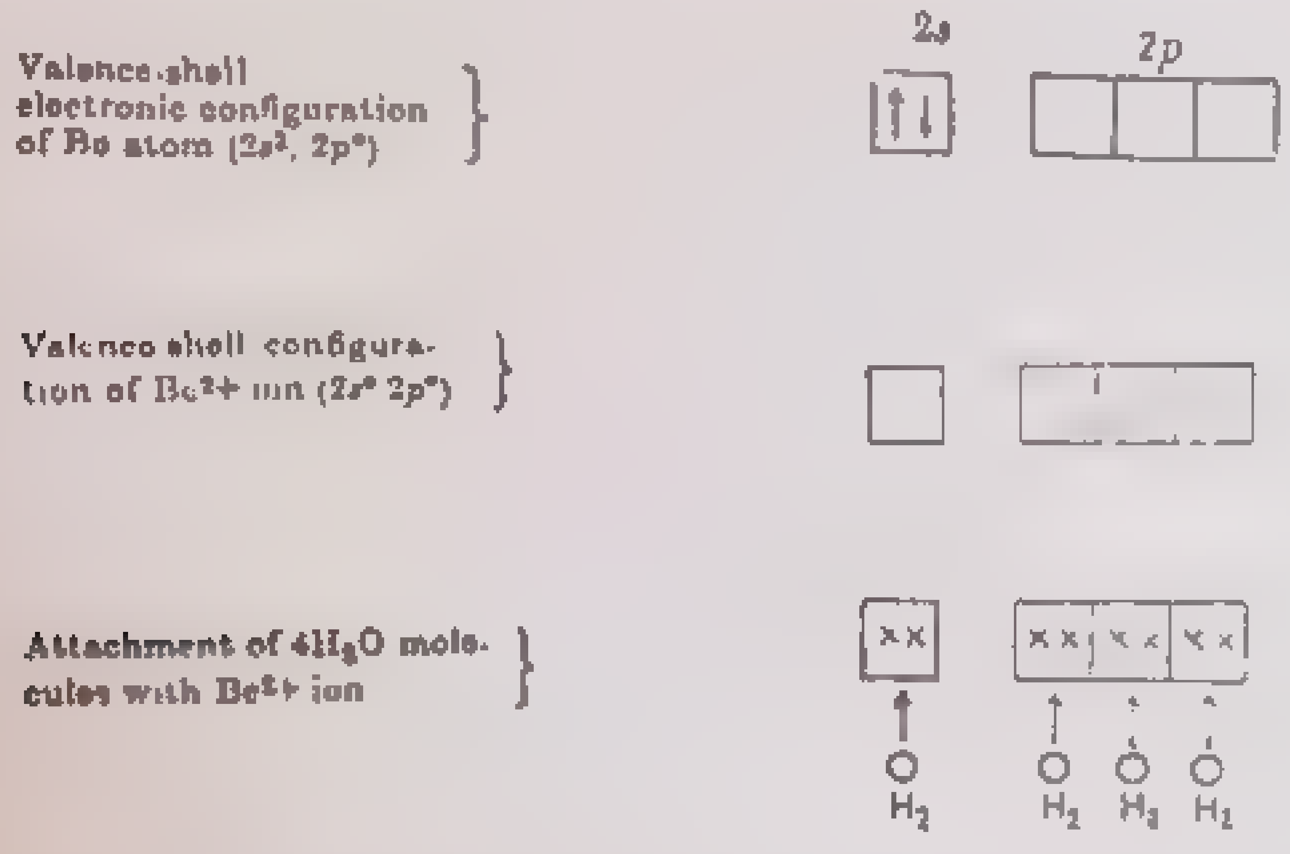
$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

The carbide of other alkaline earth metals are decomposed by water to form acetylene (C_2H_2). For example

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

9. ***Behaviour of nitrides:*** Be_3N_2 is volatile while the nitrides of other alkaline earth metals are non volatile.

10. ***Number of molecules of water of crystallisation:*** The salts of Be^{2+} ion cannot have more than four molecules of water of crystallisation while other alkaline earth metals have more than four molecules of water of crystallisation. It is because, in case of Be^{2+} ion there are only four orbitals. One orbital can accept only one lone pairs of electrons denoted by O-atoms of the water molecules as shown below



On the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell. Thus, Mg in Mg^{+2} state is

i.e. $\;_{12}Mg^{+2}\ 1s^2\ 2s^2\ 2p^6\ 3s^0\ 3p_x^0\ 3p_y^0\ 3p_z^0\ 3d_{xy}^0\ 3d_{xz}^0\ 3d_{yz}\ 3d\ 3d$

11. ***Formation of complex compounds:*** Be^{2+} ion, on account of its small size forms stable complex compounds like $[BeF_3]^-$, $[BeF_4]^{2-}$ The M^{2+} ions derived from other alkaline earth metals form very few complex compounds

QUICK QUIZ-9

(1) *Among the alkaline earth metals atoms which has the highest ionization potential?*

Be has the smallest size among alkaline earth metals so it has the highest ionization potential

(2) *Explain why Ca, Sr, Ba, and Ra are places in one group of the periodic table*

The general valence shell electronic configuration of all these elements is ns^2. Thus due to ... configuration these elements show similar chemical properties. Hence these are placed in one group

(3) *Explain the following*

(a) *Alkaline earth metals form M^{2+} ions but no M^+ ions.*

Alkaline earth metals have two valence electrons. Both these electrons have quite low ionization energy ... both these electrons are lost easily. Hence they form M^{2+} ions instead of M^+ ions

(b) Although [illegible]
potenti[illegible]

(c) Bery[illegible]

[illegible]

One the other hand [illegible]
one 3s, three 3p and two 3d orbitals belonging to their ou[illegible]

(d) *The solubility of the sulphates of alkaline earth metals decreases* [illegible] *increases on moving down the group*

- In hydroxides, OH^- is a small anion. So [illegible] metals only. Here, lattice energy [illegible] group so the lattice energy decreases and [illegible]
- In sulphates, SO_4 ion is common, which is a quite bigger anion [illegible] lattice energy. So down the group hydration energy decreases due [illegible] alkaline earth metals thus solubility of sulphates decreases down the group.

(e) *The thermal stability of carbonates of alkaline earth metals increases in atomic numbers*
It is because in small size ions the gain in electrostatic attraction [illegible] case of large cation the gain in electrostatic attraction is relatively [illegible] Since the size of cation increases down the group therefore stability also increases.

(f) *Alkaline earth metals salts impart colour to the Bunsen flame*
In alkaline earth metals, the outer electron is loosely held with the nucleus. So it can be [illegible] higher energy levels by absorbing a small amount of heat energy. When this excited electron [illegible] original position, it gives out absorbed energy in the form of light in visible region. Different amount [illegible] absorbed in different atoms for excitation of electron. Thus, different colours are imparted by the [illegible] flame.

(g) *$MgSO_4$ is more soluble in water than $BaSO_4$.*
It is because, the SO_4^{2-} ion is common in both. This ion is a quite bigger anion. Hence hydra[illegible] overcomes the lattice energy. Since, size of Ba^{2+} ion is greater than that of Mg^{2+} ion so hydratio[illegible] Ba^{2+} ion is less than Mg^{2+} ion.

(h) *Alkaline earth metals form M^{2+} ions but not M^{3+} ions.*

- It is because, alkaline earth metals have two valence electrons. By the removal of both electrons [illegible] earth metals get the configuration of noble gases and thus they form M^{2+} ions.
- It becomes very difficult to remove the third electron from a noble gas configuration ion. Therefore [illegible] ionization energy of alkaline earth metals is quit high. Hence they cannot form M^{3+} ions.

How do the elements of group IIA differ from alkali metals

See Page 57 for the difference

The hydroxides of group IIA metals are weaker than those of group IA metals

Group IIA [illegible]

The carbonates of group IIA metals are less stable [illegible]

[illegible]

KOH is stronger base than $Ba(OH)_2$

[illegible]

GROUP 4 ELEMENTS

The Group 4 [illegible]

ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

MELTING POINTS AND BOILING POINTS

- The [illegible]
- The m[illegible] regular [illegible]
- The de[illegible] forces [illegible] of C and Si are [illegible] giant molecules
- The melting point [illegible] distorted 1 2 [illegible] values in the [illegible]

BRITTLENESS

If a substance shatters [illegible]

- Carbon as diamond [illegible] hammer, it shatters. Th[illegible]
- Silicon, germanium and [illegible]
- However, white tin and lead [illegible] of the metallic bonds. Thus [illegible]
- Lead in particular is a [illegible]

ELECTRICAL CONDUCTIVITY

- Carbon as diamond does not conduct [illegible] to move
- Silicon, germanium and grey tin are se[illegible]
- White tin and lead are normal metallic conductors [illegible]
- Thus, electrical conductivity increases down the group [illegible] carbon as diamond to the typically metallic behaviour [illegible]

ELECTRONEGATIVITY

- Carbon is the most electronegative elements of this group
- The electronegativities decrease with increase of atomic number [illegible] irregularity is due to the filling of the d-orbital in case of Ge and S[illegible]

IONIZATION ENERGIES

The ionization energy values decrease down the group form C to Pb However, the decrease is not regular

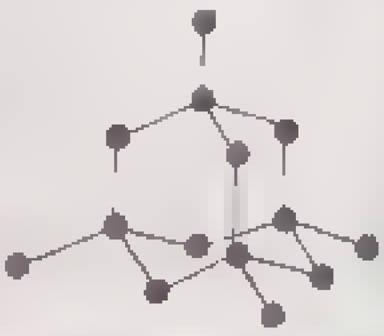
The irregularity is due to the filling of the d orbitals in case of Ge and Sn and f orbitals in case of Pb. Since d and f-orbitals have poor shielding effect so they cannot shield the valence electron effectively. Hence, the pattern becomes irregular

Remember!
The similar explanation can be given to irregularities in atomic radii, electronegativity etc

THE TREND FROM NON-METAL TO METAL IN THE GROUP 4 ELEMENTS

STRUCTURES OF THE ELEMENTS

The metallic character increases down the group in Group 4 elements



- Carbon at the top of the Group has giant covalent structures It has two common allotropes, diamond and graphite
- Diamond has a three dimensional structure of carbon atoms each bonded covalently to four (4) other atoms as shown in the figure
- This same structure is found in silicon and germanium and in one of the allotropes of tin, which is "grey tin" or "alpha-tin"
- The common allotrope of tin "white tin" or "beta tin" is metallic In this form atoms are held together by metallic bonds Its structure is a distorted close packed arrangement In close packing each atom is surrounded by twelve (12) near-neighbours.
- Thus, a clear trend is found down the group from the typical covalency in non-metals to the metallic bonding in metals
- The change-over in the two entirely different structures of tin is the exception

Exercise Q3 (viii) Explain the trends in oxidation states with suitable examples

OXIDATION STATE

The apparent charge positive or negative on an atom in a substance is called its oxidation state or oxidation number

(a) INERT PAIR EFFECT AND POSITIVE OXIDATION STATES

- Carbon and silicon commonly show +4 oxidation states
- Germanium commonly shows both +2 and +4 oxidation states
- Tin and Pb commonly shows +2 oxidation states.

- When two np^2 electrons are lost from the ns^2np^2 configuration, the elements show +2 oxidation states.
- The two electrons in ns^2 are not lost in the formation of M^{2+} cations. This pair of ns^2 electrons is called inert pair of electrons.
- The stability of +2 oxidation state increases from Ge^{2+} to Pb^{2+} i.e. $Ge^{2+} < Sn^{2+} < Pb^{2+}$

- When all the four ns^2np^2 electrons are lost, the elements show +4 oxidation state, i e M^{4+} cations are formed
- The stability of +4 oxidation state decrease down the group i.e. $Ge^{4+} > Sn^{4+} > Pb^{4+}$

➤ *Compounds of Ge^{2+} are less stable than those of Ge^{4+}. Hence the compounds of Ge^{2+} are readily changed/oxidized into those of Ge^{4+} Thus, compounds of Ge^{2+} act as strong reducing agents while those of Ge^{4+} act as oxidizing agents.*

Ge^{2+} compounds → Ge^{4+} compounds
Less stable / **Reducing agent** → **More stable** / **Oxidizing agent**

Remember! A reducing agent reduces other but is itself oxidized
e g. Ge^{2+} gives electrons to form Ge^{4+} (itself oxidized). The electrons lost by Ge^{2+} are added to some other species So that species is reduced Hence Ge^{2+} is a reducing agent

- Similarly, it can be shown that the compounds of Sn^{2+} are [illegible] Sn^{4+}. [illegible] Sn^{2+} act as strong reducing agents while those of Sn^{4+} act as [illegible].

  Sn^{2+} compounds $\rightarrow$ Sn^{4+} compounds
  Less stable — **More stable**
  Reducing agent — **Oxidizing agent**

- Similarly, Pb^{2+} compounds are more stable than those of Pb^{4+}. Thus, compounds of Pb^{4+} act as strong oxidizing agents while those of Pb^{2+} act as reducing agents.

  Pb^{2+} compounds $\rightarrow$ Pb^{4+} compounds
  More stable — **Less stable**
  Reducing agent — **Oxidizing agent**

- Thus, the order of stability of M^{2+} and M^{4+} cations of Ge, Sn and Pb is

  $Ge^{2+} < Ge^{4+}$; $Sn^{2+} < Sn^{4+}$; $Pb^{2+} > Pb^{4+}$

(b) NEGATIVE OXIDATION STATE

- Since the electronegativities of these elements are low, they do not have much tendency to form the negative ion.
- However, carbon forms C^{4-} and C_2^{2-} ions in certain compounds

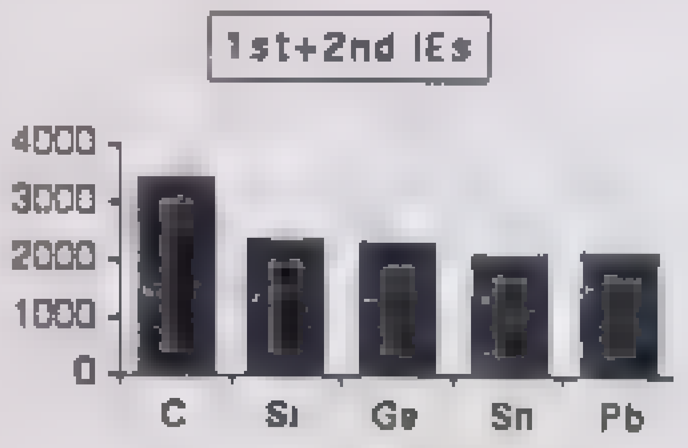
Examples:

Be_4C_2 or Be_2C (Be^{2+} and C^{4-} ions) Al_4C_3 (Al^{3+} and C^{4-} ions) $NaCH_3$ (Na^+, C^{4-} and H^+ ions)
NaC_2 (Na^+ and C_2^{2-} ions) CaC_2 (Ca^{2+} and C_2^{2-} ions)

Exercise Q3 (ix) Discuss the inert pair effect in the:
(a) formation of ionic bonds (b) formation of covalent bonds

THE INERT PAIR EFFECT IN THE FORMATION OF IONIC BONDS

- If the elements in Group 4 form 2+ ions, they will lose the p^2 electrons, leaving the s^2 pair unused **e.g.** to form a lead(II) ion, lead will lose the two 6p electrons, but the 6s electrons will be left unchanged, which is the "inert pair"



- Generally, ionization energies decreases down the group. However, in Group 4, this does not quite happen
- The total ionization energy needed to form the 2+ ions are shown in the figure in kJ mol^{-1}. The figure shows there is a slight increase between tin and lead. It shows that it is slightly more difficult to remove the **p**-electrons from lead than from tin

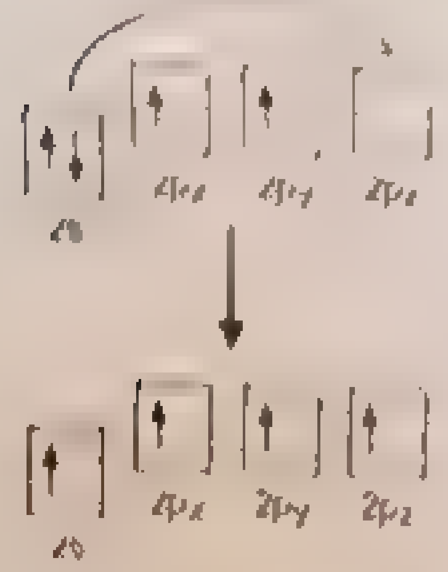
- The total ionization energy needed to form the 4+ ions are shown in the figure in kJ mol^{-1}. The difference between tin and lead is more prominent. The relatively large increase between tin and lead must be because the $6s^2$ pair is significantly more difficult to remove in lead than the corresponding $5s^2$ pair in tin. *It can be explained by Theory of Relativity*

Relativistic Contraction
With the heavier elements like lead, ***relativistic contraction*** *of the electrons tends to draw the electrons more closer to the nucleus than expected. Thus, they are more difficult to remove. The heavier the element, the greater this effect. This affects s-electrons much more than p-electrons.*

In the case of lead, the relativistic contraction makes it more difficult to remove the 6s electrons [illegible]. The energy releasing in other process like lattice ethalpy and hydration enthalpy are not enough [illegible] this extra energy. It means for lead it is not energetically favourable to form 4+ ions

THE INERT PAIR EFFECT IN THE FORMATION OF COVALENT BONDS

- Before carbon ...



- Thus there becomes 4 unpaired electrons. These undergo hybridization to form 4
- The energy for promotion of s-electron is supplied because the carbon can ... covalent bonds. Each covalent bond formation releases energy which is more ...
- The lead cannot do this. It is because bond energies decreases down the Group ... the bonding pair goes away from the two nuclei and better screened from them.

  e.g., the energy released when two extra Pb-X bonds are formed may no ... compensate for the extra energy needed to promote a 6s electron into the ...
- This becomes even more difficult, if the energy gap between the 6s and 6p orbitals was in... relativistic contraction of the 6s orbital

CHEMICAL PROPERTIES OF THE ELEMENTS OF GROUP 4 ELEMENTS

THE CHLORIDES OF CARBON, SILICON AND LEAD

STRUCTURES AND STABILITY

STRUCTURES

CARBON, SILICON AND LEAD TETRACHLORIDES

- These all have the formula MCl_4.
- They are all simple covalent molecules with a typical tetrahedral shape
- All of them are liquids at room temperature. However, at room temperature lead(IV) chloride ... decompose to give lead(II) chloride and chlorine gas

Lead(II) chloride, $PbCl_2$

- It is a white solid
- Its melting point is 501°C
- It is very slightly soluble in cold water, but more soluble in hot water
- It is mainly ionic in character

STABILITY

- The most st...
- This oxidation st... spl up t...
- However the ... oxidation st...
- Lead ... gas

easy reduction of lead from +4 to +2

PbO₄ ⟶ PbO₂ + C

REACTION WITH WATER (HYDROLYSIS)

The hy...

Step-I

- In this st...
- These att... unstab...

Step-II

- In this st... the central ele...

Tetrahalides of C are not hydrolysed while those of Si, Ge and Sn get readily hydrolysed

- The C ... is unable to ... unstable ...
- On the other han... tetrahalides get re...
- Ease of hydrolys... the central atom. Thus ...
- It must be noted howev... sufficient energy is provided for the reaction to occur e.g. ... steam is used.

Superheated st...

$$CCl_4 + H_2O \text{ (superheated steam)} \rightarrow COCl_2 + 2HCl$$

- Hydrolysis of tetrahalides of Pb follows essent... compounds of Pb. Some decomposition of $PbCl_4$ ...

$$PbCl_4 \rightarrow PbCl_2 + Cl_2$$

- $PbCl_4$ is hydrolysed by H_2O as follows

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$$

- The tetrahalides of Si, Ge, Sn and Pb reac... $[SiF_6]^{2-}$, $[GeX_6]^{2-}$ e.g.

$$SiF_4 + 2F^- \rightarrow [SiF_6]^{2-}$$

- The tetrahal... of C are exception. They donot form such ...

OXIDES

- There is a large difference between the physical properties of ... known as silicon(IV) oxide or silica)
- Carbon dioxide is a gas whereas silicon dioxide is a hard high-me...
- The other dioxides in Group 4 are also solids. This is also due ... dioxide and the dioxides of the rest of the Group

THE STRUCTURE OF CARBON DIOXIDE

- The dipole moment of carbon dioxide is zero. Therefore ...

THE STRUCTURE OF SILICON DIOXIDE

- It is a macromolecular compound, in which silicon and oxygen atoms are linked ... tetrahedral basic unit
- In crystobalite, these units are joined as in diamond, while in quartz and ... around an axis
- Due to this structure silicon dioxide is non-volatile and hard unlike carbon dioxide

Similarity between structure of silicon dioxide and carbon dioxide

- Triatomic molecules of silicon dioxide and carbon dioxide, carbon and silicon are similar in having
  (i) 4 valence electrons
  (ii) 4 covalent bond formation

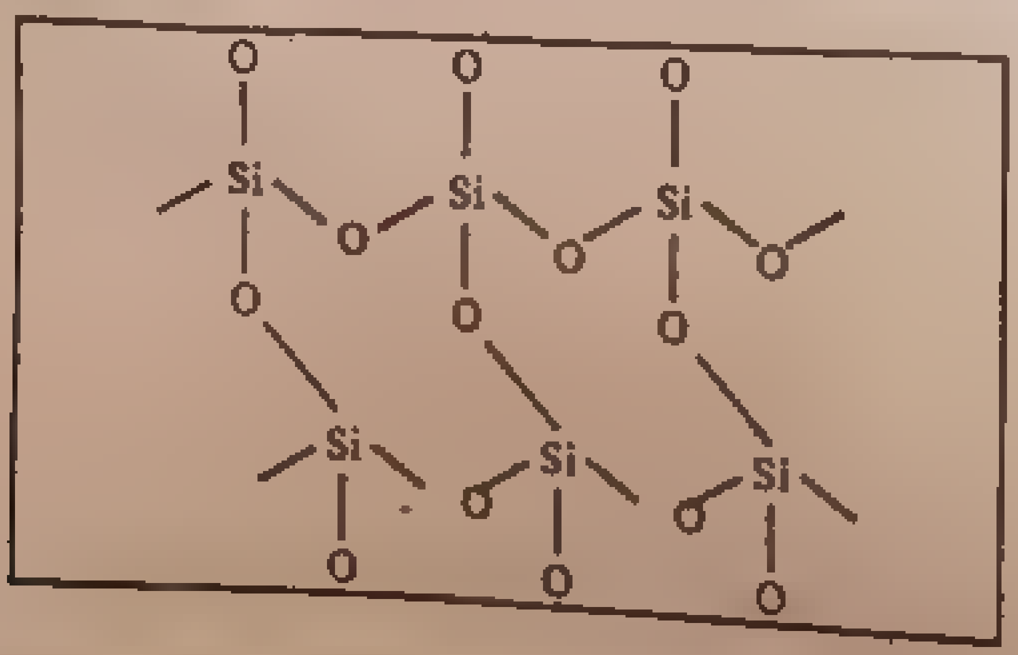
Differences between structure of silicon dioxide and carbon dioxide

But they show a lot of difference in their physical properties. It is due to the fact that

(i) Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more ... atoms.

(ii) Silicon from only single bond with oxygen atoms while carbon forms double bonds.

(iii) Carbon forms a linear molecule of CO_2 with two oxygen atoms. While silicon atom is bound to four ... atoms in a tetrahedral structure which result in the formation of silicon dioxide crystal. The simplest ... for silica is SiO_2. However the whole crystal of silicon can be considered as one molecule



Exercise Q3 (x) Discuss in detail acid-base trend in group 4 oxides

THE ACID-BASE BEHAVIOUR OF THE GROUP 4 OXIDES

- The oxides of the elements at the top of Group 4 are acidic
- The acidity of the oxides decreases down the Group
- Towards the bottom of the Group, the oxides become more basic. However, they do not lose their acidic character completely. Thus they become amphoteric
- An oxide which can show both acidic and basic properties is said to be ***amphoteric***
- The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom

CARBON AND SILICON OXIDES

CARBON MONOXIDE

- It is treated as if it is a neutral oxide. However, it is very slightly acidic
- It does not react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate

$$NaOH + CO \rightarrow HCOONa$$

- This reaction shows that it must be acidic

CARBON AND SILICON DIOXIDES

These are both weakly acidic

Reactions with water

- Silicon dioxide does not react with water. It is due to the difficulty of breaking up the giant covalent structure
- Carbon dioxide does react with water to a slight extent to produce hydrogen ions (strictly, hydroxonium ions) and hydrogencarbonate ions

$$H_2O_{(l)} + CO_{2(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

- The solution of carbon dioxide in water is sometimes known as carbonic acid. It is actually about 0.1% of the carbon dioxide has actually reacted. The position of equilibrium is well to the left hand side

Reactions with bases

- Carbon dioxide reacts with sodium hydroxide solution in the cold to [illegible] sodium hydrogencarbonate solution
- The ratio of both depends upon the relative amounts of reactants

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

$$NaOH + CO_2 \rightarrow NaHCO_3$$

- Silicon dioxide reacts only with hot and concentrated sodium hydroxide sol[illegible] formed.

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

- The famous reaction in the blast furnace extraction of iron is also with a basic species, CaO
  - ✓ In this reaction calcium oxide (from the raw material limestone [illegible] liquid slag called calcium silicate.
  - ✓ This reaction also shows the acidic behaviour of silicon dioxide reac[illegible]

$$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)}$$

GERNAMIUM, TIN AND LEAD OXIDES

THE MONOXIDES

All of these oxides are amphoteric they show both basic and acidic properties

The basic nature of the oxides

- These oxides all react with acids to form salts. **e.g.**, they all react with concentrated ...

$$MO_{(s)} + 2HCl_{(aq)} \rightarrow MCl_{2(aq)} + H_2O_{(l)}$$

where M can be Ge and Sn However, lead shows a different behaviour

- Lead(II) chloride is fairly insoluble in water and instead of getting a solution ... over the lead(II) oxide by use of *dilute* hydrochloric acid Thus reaction is stopped

$$PbO_{(s)} + 2HCl_{(aq)} \rightarrow PbCl_{2(s)} + H_2O_{(l)}$$

- However, with *concentrated* hydrochloric acid it does not happen In concentrated ... chloride ions react with the lead(II) chloride to produce soluble complexes such as $PbCl_4^{2-}$ ... complexes are soluble in water and so the problem disappears.

$$PbCl_{2(s)} + 2Cl^-_{(aq)} \rightarrow PbCl_4^{2-}{}_{(aq)}$$

The acidic nature of the oxides

- All of these oxides also react with bases like sodium hydroxide solution

$$MO_{(s)} + 2OH^-_{(aq)} \rightarrow XO_2^{2-}{}_{(aq)} + H_2O_{(l)}$$

- Lead(II) oxide, for example, would react to give PbO_2^{2-} [plumbate(II) ions]

THE DIOXIDES

These dioxides are again amphoteric. Thus these shows both basic and acidic properties

The basic nature of the dioxides

- The dioxides react with concentrated hydrochloric acid first to give compounds of the type MCl_4

$$MO_2 + 4HCl \rightarrow MCl_4 + 2H_2O$$

- These will react with excess chloride ions in the hydrochloric acid to give complexes such as XCl_6^{2-}

$$XCl_4 + 2Cl^- \rightarrow XCl_6^{2-}$$

- In the case of lead (IV) oxide, the reaction is carried out with ice cold hydrochloric acid It is because if the reaction is done any warmer, the lead (IV) chloride decomposes to give ... and chlorine gas This shows the preferred oxidation state of lead being +2 rather than +4

The acidic nature of the dioxides

- The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complex form $[M(OH)_6]^{2-}$

$$XO_{2(s)} + 2OH^-_{(aq)} + 2H_2O_{(l)} \rightarrow [X(OH)_6]^{2-}{}_{(aq)}$$

- Some sources suggest that the lead(IV) oxide needs molten sodium hydroxide In that case the eq... different

$$PbO_{2(s)} + 2NaOH_{(l)} \rightarrow Na_2PbO_{3(s)} + H_2O_{(g)}$$

QUICK QUIZ-10

GROUP 7-ELEMENTS: (HALOGENS)

ATOMIC AND PHYSICAL PROPERTIES

TRENDS IN ATOMIC RADIUS

Exercise Q3

physical properties

TRENDS IN ELECTRONEGATIVITY

TRENDS IN FIRST ELECTRON AFFINITY

However, the electron affinity

TRENDS IN MELTING AND BOILING POINTS

- The melting and boiling points

  It is because

  between molecules

- F_2 and Cl_2 are gases at

BOND ENTHALPIES (BOND ENERGIES OR BOND STRENGTHS)

- Bond enthalpy is the heat

  starting from the original substance

- For chlorine $Cl_{2(g)}$ it is the heat energy

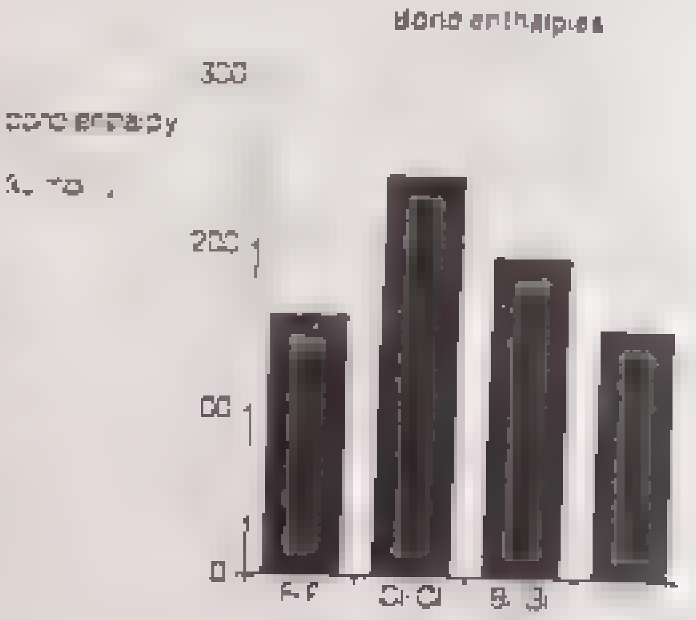
$$Cl\text{–}Cl_{(g)} \rightarrow 2Cl_{(g)}$$

- For bromine the reaction is st . from gaseous bromine molecules to separate gase...

$$Br\text{–}Br_{(g)} \rightarrow 2Br_{(g)}$$

Gas not Liquid

BOND ENTHALPY IN THE HALOGENS, $X_{2(g)}$



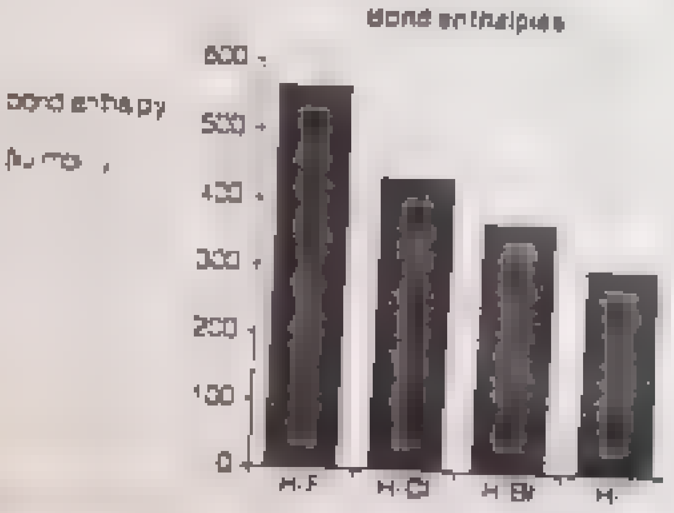
The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases down the group due to increase in atomic size except the F-F bond

F-F bond has very low dissociation energy. It is due to following reasons

(I) It is due to very small F-F bond length than other X-X bond lengths. So the F atoms in F_2 molecule repel each other and thus the dissociation of F_2 molecule into F atoms becomes easy

(II) X-X bond in Cl_2, Br_2 and I_2 molecules is stronger than F-F bond in F_2 molecule. It is due to the possibility of the formation of multiple bonds in X-X bond with d- orbitals.

BOND ENTHALPIES IN THE HYDROGEN HALIDES, $HX_{(g)}$



The bond enthalpies of HX decreases down the group

It is because, as the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less and the bond gets weaker. So the bond enthalpies of HX decreases down the group

STRENGTH OF HALOGENS AS OXIDIZING AGENTS: $F_2>Cl_2>Br_2>I_2$

FACTS:

- A substance that has a tendency to accept one or more electrons is said to show oxidizing property
- The halogens due to high electron affinity values have a great tendency to accept electron and hence act as strong oxidizing agent
- The oxidizing property of a halogen molecule, X_2 is represented by:

$$X_2 + H_2O \rightarrow HX + HOX$$ *(in this reaction, X takes electrons)*

- During this reaction energy is released. This energy is made up from different energies like that of fusion vaporisation etc
- The values of energy decrease from F_2 to I_2. Thus, the oxidizing power of halogens also decreases in the same direction. Thus, order of oxidizing power is

$$F_2 > Cl_2 > Br_2 > I_2$$ *(weakest oxidizing agents).*

- Since F_2 is the strongest oxidizing agent in the series, it will oxidize other halide ions to halogens in solution or when dry. **i.e.,** F_2 displaces other halogens from their corresponding halides

$$F_2 + 2X^- \rightarrow 2F^- + X_2$$

- Similarly Cl_2 will displace Br^- and I^- ins from their solutions and Br_2 will displace I^- ions from their solutions

$$Cl_2 + 2X^- \rightarrow 2Cl^- + X_2$$

$$Br_2 + 2X^- \rightarrow 2Br^- + X_2$$

THE ACIDITY OF THE HYDROGEN HALIDES

- All the halogen acids in the gaseous states are essentially covalent

However, in the aqueous solution they ionise to give solvated proton (H_3O^+) and hence acts as acids

$$H_2O + HX \rightarrow H_3O^+ + X$$

- HF ionises only slightly while HCl, HBr, and HI ionise completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI

The order of acidity is

HF *(weakest acid)* < HCl < HBr < HI *(strongest acid)*

- The weakest acidic nature of HF is due to the fact that the dissociation energy of H-F bond in HF molecule is the highest. Hence this molecule has least tendency to splits up into H and F ions in aqueous solution
- The above order of the acidic strength of HX acids can also be explained on relative order of the basicity of the conjugate bases of these acids. The order is $F^- > Cl^- > Br^- > I^-$. Since a stronger conjugate base means a weaker acid, therefore the order of acidity of HX acids is HF < HCl < HBr < HI
- The hydrides show no acidic character when perfectly dry.

HALIDE IONS AS REDUCING AGENTS
TRENDS IN REDUCING STRENGTH ABILITY OF HALIDE IONS

(THE REDOX REACTIONS BETWEEN HALIDE IONS AND CONCENTRATED SULPHURIC ACID)

- Fluorides and Chlorides do not reduce concentrated sulphuric acid
- **With bromide ions**
  - ✓ The bromide ions are strong enough reducing agents to reduce the concentrated sulphuric acid
  - ✓ In the process the bromide ions are oxidized to bromine

$$2Br^- \rightarrow Br_2 + 2e^-$$

  - ✓ The bromide ions reduce the sulphuric acid to sulphur dioxide gas
  - ✓ This is a decrease of oxidation state of the sulphur from +6 in the sulphuric acid to +4 in the sulphur dioxide

$$H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$$

- Combine these two half-equations to give the overall ionic equation for the reaction

$$H_2SO_4 + 2H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_2O$$

- **With iodide ions**
  - ✓ Iodide ions are stronger reducing agents than bromide ions are
  - ✓ They are oxidized to iodine by the concentrated sulphuric acid

$$2I^- \rightarrow I_2 + 2e^-$$

- The reduction of the sulphuric acid is more complicated than before. The iodide ions are powerful enough reducing agents to reduce it
  - ✓ first to sulphur dioxide (sulphur oxidation state = +4
  - ✓ then to sulphur itself (oxidation state = 0)
  - ✓ and all the way to hydrogen sulphide (sulphur oxidation state -2
  - The most important of this mixture of reduction products is probably the hydrogen sulphide. The half equation for its formation is:

$$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$$

  - Combining these last two half-equations gives

$$H_2SO_4 + 8H^+ + 8I^- \rightarrow 4I_2 + H_2S + 4H_2O$$

SUMMARY

- Fluoride and chloride ions won't reduce concentrated sulphuric acid
- Bromide ions reduce the sulphuric acid to sulphur dioxide. In the process, the bromide ions are oxidized to bromine
- Iodide ions reduce the sulphuric acid to a mixture of products including hydrogen sulphide. The iodide ions are oxidized to iodine
- Reducing ability of the halide ions increases as you go down the Group

Explanation

- When a halide ion acts as a reducing agent, it gives electrons to something else. That means that ion itself has to lose electrons
- The bigger the halide ion, the further the outer electrons are from the nucleus and the more screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons down the Group because there is less attraction between the outer electrons and the nucleus

QUICK QUIZ-11

(1) Give reasons of the following

- ***HI is stronger acid than HF.***

It can be explained on following bases

(i) In HF molecules are Hydrogen-bonded in a zigzag manner. Thus H-atom is entrapped between two F atoms as shown in the fig. So H^+ ion cannot be donated easily

(ii) The bond energy of H-F bond is considerably greater than H-I bond. Thus HF cannot donate its H^+ ions easily

(iii) The conjugate base of HF is F^- ion which is a stronger base than I^- ion. Thus its corresponding acid, HF will be weaker than HI

Hence, HI is a stronger acid than HF

- ***Although H-bonding in HF is stronger than that in H_2O, H_2O has much higher b.pt.***

It is because, HF can make one hydrogen bond per molecule while water can make two hydrogen bond per molecules. So, due to strong hydrogen bonding in water, it has higher boiling point than HF

- ***The acidic character of hydrides of VIIA elements increases on descending g the group.***

✓ It is because down the group bond energy of H-X bond decreases, so the ease of donation of proton increases

✓ Moreover, the order of basicity of their conjugate bases is $F^- > Cl^- > Br^- > I^-$. Since, a stronger conjugate base means a weaker acid, therefore, the order of acidity of HX acids is HF < HCl < HBr < HI

Hence acidity increases down the group.

(2) Illustrate the oxidizing properties of halogens by giving example of two typical reactions.

A substance that has a tendency to accept one or more electrons is said to show oxidizing property

The halogens have high electron affinity values and also high hydration energy values of their ions. Thus they have a great tendency to accept electron and hence act as strong oxidizing agent

e.g. F_2 displaces other halogens from their corresponding halides.

$$X_2 + H_2O \rightarrow HX + HOX$$

(3) Arrange the halogens in the decreasing order of their oxidizing power.

The order of oxidizing power is

$F_2 > Cl_2 > Br_2 > I_2$ *(weakest oxidizing agents).*

Q. Give reasons for the following

(a) Chlorine is a stronger oxidizing agent than iodine

It is due to two reasons [illegible]

- The electron [illegible]
- The hydration [illegible] solution. Th[illegible] main factor.

It means, the chlorine [illegible] stronger oxidizing agent [illegible]

(b) Halogens are the best oxidizing agents

A substance that has a tendency to [illegible]

The halogens have high e[illegible] have a great tendency to accept elect[illegible]

e.g.

$$X_2 + H_2O \rightarrow HX + HOX$$

(c) Fluorine is a batter oxidizing than chlorine

It is due to two reasons

- The bond dissociation ene[illegible]
- The main factor, however, is hydration [illegible] so it will form readily in solution. Thus fluorine [illegible] Hence, fluorine is a much stronger oxidizing agent th[illegible]

(d) Electronegativity of halogens decreases in the order F > Cl > Br > I

It is due to increase in size of halogens down the group.

Due to increase in size, the distance of bonding pair increases from [illegible] pairs are less strongly attracted and so the electronegativity decreases.

SOCIETY, TECHNOLOGY AND SCIENCE

Food and Beverage Canning

History

As early as 1940, can manufacturers began to explore adapting c[illegible] important points were investigated for their production.

(1) The can had to be strengthened to accommodate highe[illegible] (especially during warm summer months). It means increasing the th[illegible] Otherwise, distortion of the end [illegible] strain the seal [illegible] storage and transit.

(2) Another concern for the new beverage can was its shelf life. Even sma[illegible] the can could impair the drinking quality of both beer and soft drinks.

Fortunately, beer, which is only mildly acidic, is relatively non[illegible] has a limited shelf life of about three months in any package.

In contrast, the food acids, including carbonic, citric and phosph[illegible] corrosion of exposed tin and iron in the can.

The consequences of off-flavors, color changes and leakage through the [illegible] point, the can was upgraded by improving the organic coatings used [illegible] more encasing.

ELEMENTS/METALS THEIR MINING AND EXTRACTION

Different elements metals are not obtained such rather these are obtained after passing through different steps. These steps are:

(1) *Mining and enrichment*
(2) *Reduction*
(3) *Refining and Casting*

In fact some special methods are used to obtain each metal from its ores and to develop it into useful articles. However, few steps are common in the metallurgy of every metal. These are follows

(1) MINING

(i) Crushing

- Obtaining ores by digging the rocks and hills is called mining
- This work is done by engineers and laborers with the help of machines
- But before this work it is confirmed by survey and analysis that obtaining metals from this is ... or not

(ii) Grinding

- Breaking of rocks and larger stones into smaller size stones is called crushing
- This is done by jaw crushers

(iii) Hand Picking, Jugging and Shaking

- In Pakistan and other under developed countries where labour is cheap metallic stones are picked and separated by hands.
- Heavy metals are separated from useless material i.e. gangue, by shaking with chaage
- In some countries this process is done by pressurized water

(iv) Magnetic Separation

- The ground ore is passed over a magnetic belt which separates the magnetic metal from gangue
- This process is sued for metals which have magnetic properties like iron.

(2) REDUCTION

- For the complete separation of a metal from gangue, ores are heated at high temperature
- At its melting pint, molten metal is separated from solid gangue
- Different metals are mixed with different compounds according to the type of impurities present metal ore
- Then they are passed through the process of reduction.
- The process of reduction is carried out in the blast furnace

Blast Furnace

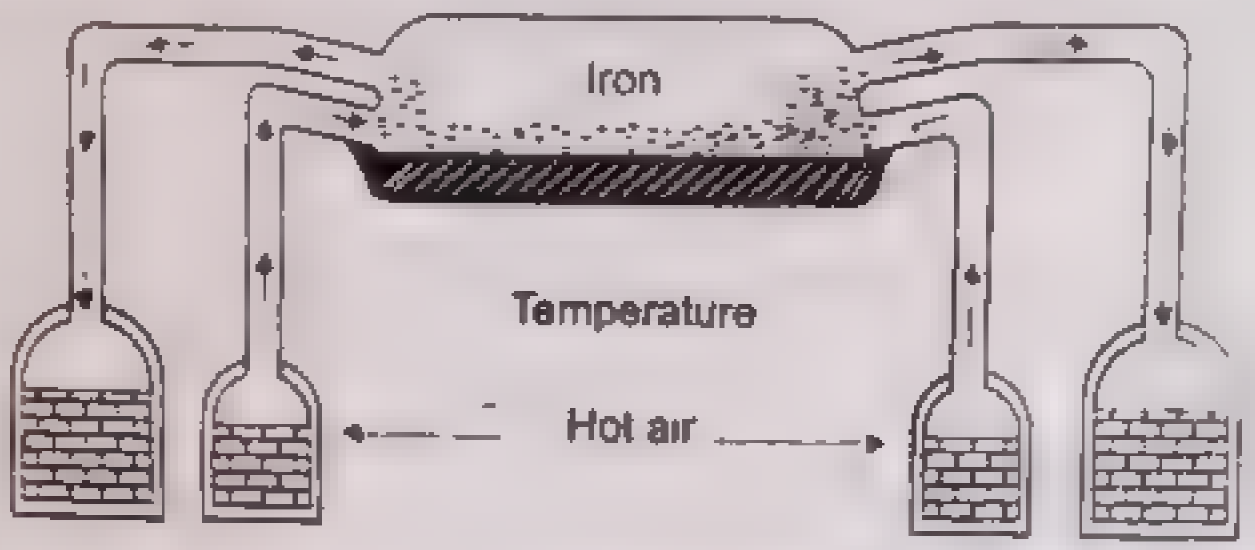
- It is lined inside with fire bricks.
- Its height and capacity are kept according to the requirement.
- Hot gases enter from lower side and ores are charged from the tope of the furnace
- Temperature is maintained at 1500°-3000°C.
- This furnace is usually used for iron and copper metallurgy

REFINING OF METALS

Metals extracted in the above process are further refined by the following process

Open-Hearth Process

- A fire furnace is used to remove the impurities of metal
- It is lined inside with fire bricks and is just like a room
- Burning gases are entered from one side and exhaust gases are removed from the opposite end. The process is operated form opposite ends after an interval. Metals melt in a shorter time by this two way heating



APPLICATIONS OF BLEACHING POWDER.

- Bleaching powder is actually a mixture of calcium hypochlorite $Ca(OCl)_2$ and the basic chloride $CaCl_2.H_2O$ with some slaked lime, $Ca(OH)_2$
- Bleaching powders take time to dissolve in water and longer to work. But it has a ... in comparison to liquid bleaches and can be used on items like upholstery, carpet and some ...
- However, bleaching powder should never be combined with ammonia or ... cause fading
- Bleaching powder is used for bleaching cotton and linen. It is also used ... disinfectant sprays, moss and algae removers, and weedkillers
- Bleaching powder is highly effective for cleaning inside the home and outdoors
  - ✓ It can be used for removing mildew from fabric, cleaning countertops and ... between tiles, bathmats and shower curtains
  - ✓ Outside, the agent can be used on plastic furniture, unpainted ... eliminate mildew and other stubborn stains
- Bleaching powder can be used to safely disinfect
  - ✓ It can sterilize many things around the home including secondhand ... and baby toys and furniture
  - ✓ Bleaching powder is a highly effective means of returning the luster ... Glassware can regain its sparkle by adding a small amount of ... washing glasses.
- Gardening
  - ✓ To kill any annoying weeds growing from cracks ... bleaching powder and water is applied
  - ✓ Moss and algae on garden walkways can be easily eliminated ... diluted in water.
  - ✓ Powdered bleach is also useful for sanitizing garden ...
  - ✓ Adding powdered bleach to the water of cut flowers ... the growth of bacteria in the vase

[illegible]

COMMERCIAL USES OF HALOGENS

1. [illegible]
2. [illegible]
3. [illegible]

$UF_4(s) + F_2(g) \rightarrow UF_6(s)$

4. [illegible] ...nts, aerosol [illegible]

One of the most important fluorocarbons is poly (tetrafl[illegible] ...equently sold under the trade name Fluon or Teflon.

IODINE DEFICIENCY AND GOITER

Iodine Deficiency

- [illegible] that is needed for the production of thyroid hormone. The human body cannot synthesize iodine so it is an essential element.
- [illegible] leads to enlargement of thyroid a condition called goiter.
- [illegible] mental retardation in children and infants is observed [illegible] mothers suffered [illegible] iodine deficiency during pregnancy.
- [illegible] deficiency was common in Appalachian, north western US regions and in most of Canada. Approximately, 40% of the world's population remains at the risk of iodine deficiency.

Goiter.

- The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet.
- It results in swelling in neck.
- It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism).
- A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

FLUORIDE DEFICIENCY AND TOXICITY

FLUORIDE TOXICITY

- Fluoride toxicity or fluoride poisoning is a condition in which more fluoride is taken than the amount required for normal growth, development and metabolism.
- Fluoride toxicity is characterised by a variety of signs and symptoms.

…DORIDE DEFICIENCY

Halogens and their compounds are used as ble… refr… aerosols, etc.

QUICK QUIZ-12

(1) How different metals are extracted?

Different …

(i) Mining a…

(ii) Reduction

(iii) Refining and …

(2) What problems are caused by fluoride deficiency?

Fluoride def…

(i) Brittle bones or d…

(ii) Cavities

(iii) Weakened tooth en…

(iv) Fluoride deficiency …

(3) What is goiter?

The term goiter refers to the a… in swelling in neck. A goiter … abnormally

It is important to know that the pres… malfunctioning (hypothyroidism). A g… hormone (hyperthyroidism) or even the correct a…

(4) How fluoride is useful for uranium separation

Large quantities of fluorine are used to make ura…

$$UF_4 (s) + F_2 (g) \rightarrow UF_6 (s)$$

KEY POINTS

- [illegible] of their valence shell They lose one electron of the vale [illegible]
- [illegible] valence shell
- [illegible]
- [illegible]
- [illegible] reacts with alkalies to give hydrogen. The other members [illegible]
- [illegible] give oxygen nitrogen peroxide and [illegible]
- [illegible] combination is termed as [illegible]
- [illegible] they have four electron in their valence she[illegible] two electron of which are [illegible] in p-orbitals
- The halogens are very react[illegible] halogens increase down the group, fluorine is a [illegible] but iodine is solid
- They form ionic compounds with s-block metals, covalent compound with p-block elements and comple[illegible] ions with d-block metals Fluorides are usually ionic
- They show oxidation states -1, +1, +3, +5, +7 but fluorine shows the oxidation state of -1 only
- Oxidizing power of halogens decreases down the group in the following order $F_2 > Cl_2 > Br_2 > I_2$
- Reducing power of halide ions decrease form I- to Br- Chloride and fluoride ions are not reductants

EXERCISE

Q1: Select the right answer from the choices given with each question.

i) ***Oxides and hydroxides of Group I elements are:***
(a) Acidic (b) Alkaline (c) Neutral (d) Amphoteric

(ii) ***The flame colour of sodium metal or its compounds is***
(a) bright crimson (b) violet (c) golden yellow (d) orange blue

(iii) ***When sodium burn in air, it forms sodium:***
(a) Monoxide (b) Peroxide (c) Oxide (d) Superoxide

(iv) ***The carbonates of alkali metals are not affected by heat except.***
(a) Li_2CO_3 (b) Na_2CO_3 (c) K_2CO_3 (d) Rb_2CO

(v) ***Green is characteristic flame color of***
(a) calcium (b) barium (c) strontium (d) sodium

(vi) ***All the carbonates, sulphates and phosphates of alkaline earth metals are ...*** In water
(a) sparingly soluble (b) soluble (c) insoluble (d) less soluble

(vii) ***The first ionization energy is higher for the***
a) Alkaline earth metals (b) alkali metals (c) halogens (d) noble gases

(viii) ***Which one of the element has the maximum electron affinity?***
(a) F (b) Cl (c) Br (d) I

(ix) ***Which pair has both members from same period of periodic table?***
(a) Na-Ca (b) Na-Cl (c) Ca-Cl (d) Cl Br

(x) ***Melting points and boiling points of alkali metals***
(a) decreases from top to bottom (b) increase from top to bottom
(c) first increases then decreases (d) remains unchanged

(xi) ***Which one of the following oxides is Amphoteric in nature***
(a) Rubidium oxide (b) Barium oxide (c) Antimony oxide (d) Sulphur oxide

(xii) ***Oxidizing power of halogen depends upon***
(a) energy of dissociation (b) electron affinity (c) heat of vaporization (d) [illegible]

(xiii) ***Which of following oxide is Amphoteric in nature?***
(a) MgO (b) BeO (c) CO_2 (d) SnO

(xiv) ***Select the correct increasing order of atomic radius?***
(a) Ne>O>S>Al (b) Ne<O>S>Al (c) Ne<O<S<Al (d) Ne>O>S>Al

(xv) ***Due to inert pair effect .... Oxidation state is more stable than*** For Sn and Pb
(a) 2+, 4+ (b) 1+, 4+ (c) 4+, 2+ (d) 2+, 3+

(xvi) ***Highest electron affinity is shown by?***
(a) F_2 (b) I_2 (c) Br_2 (d) Cl_2

(xvii) ***Which is the strongest reducing agent?***
(a) HF (b) HCl (c) HI (d) HBr

(xviii) ***Substance boiling at higher temperature among following is?***
(a) HI (b) HF (c) HCl (d) HBr

(xix) ***Group VII-A elements are generally called***
(a) Halogens (b) Noble gases (c) Inert gases (d) M[illegible]

(xx) ***The radioactive element in halogen group is:***
(a) Radon (b) Radium (c) Astatine (d) Bromine

ANSWERS TO MULTPLE CHOICE QUESTIONS

(i) Ans: (b) Alkaline	**(ii) Ans: (c) golden yellow**
Group I elements are highly electropositive metals. So, they form alkaline oxides and hydroxide e.g. Na_2O and NaOH	Sodium [illegible]
(iii) Ans: (b) Peroxide	**(iv) Ans: (a) Li_2CO_3**
Sodium form sodium peroxide i.e. $Na + O_2 \rightarrow Na_2O_2$	[illegible] $Li_2CO_3 \rightarrow Li_2O + CO_2$

(v) Ans: (b) barium

(vi) Ans: (d) less soluble

(vii) Ans: (d) noble gases

(viii) Ans: (b) Cl

(ix) Ans: (b) Na-Cl

(x) Ans: (a) decreases from top to bo...

(xi) Ans: (c) Antimony oxide

(xii) Ans: (d) all of above

(xiii) Ans: (b) BeO

(xiv) Ans: (c) Na<O<S<Al

(xv) Ans: (a) 2+, 4+

(xvi) Ans: (d) Cl

(xvii) Ans: (c) HI

(xviii) Ans: (b) HF

(xix) Ans: (a) Halogens

(xx) Ans: (c) Actinides

Q2: Give brief answers for the following questions.

(i) ***Although Na and P are present in the same period yet their ... different in nature Na_2O is ... while P_4O_{10} is acidic why?***

$$Na_2O + H_2O \rightarrow 2NaOH$$

Phosphorus is a non metal ... produces H_3PO_4 which is an ... formation of H_3PO_4

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

(ii) ***How acidic basic and amphoteric behaviour of oxides is explained?***

An amphoteric oxide shows both acidic and basic properties e.g. BeO

It reacts with acids to form salts

$$BeO + H_2SO_4 \rightarrow BeSO_4 + H_2O$$

It also reacts with bases to form salts

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

(i) Why the elements of group 1 are called alkali metals?

The word **alkali** [illegible] **'ashes'** [illegible]

(ii) Why all group 1 metals have low ionization energies?

In any period, Group 1 [illegible] outermost electron. Hence [illegible] e.g. Na^+, K^+ etc.

(iii) Why do the group 1 metals show strong electropositive character?

Electropositivity [illegible] electronegativity. So it is easy to remove the [illegible] energies and show electropositive character [illegible]

(iv) Why do group 1 metals show strong reducing properties?

In any period, Group 1 metals have larger size and lowest electronegativity [illegible] electrons i.e. they are easily oxidized. Thus they can reduce [illegible] is excellent reducing [illegible]

(viii) Why different colours are imparted by the atoms of the group 1 metals to the flame?

In alkali metal atoms the outermost electron [illegible] higher energy levels by absorbing [illegible] original position it gives out absorbed energy [illegible] radiations. Different amount of energy is absorbed [illegible] colours are imparted by the atoms to the flame.

(viii) Why the elements of group 2 are called alkaline earth metals?

The alkaline earth metals are given this name because they form **alkalies** [illegible] in **'earth' crust**. These include Be, Mg, Ca, Sr, Ba & Ra.

(ix) Why do the group 2 earth metals have high melting and boiling points than alkali metals?

The melting and boiling points of Group 2 elements are higher [illegible] elements have two valence electrons. So the [illegible]

(x) How do group 1 metals resemble with group 2 metals

1. Both alkali and alkaline earth metals are [illegible] s-orbital
2. Elements of both groups are highly electropositive
3. Elements of both groups do not occur free in nature
4. Hydroxides of both alkali and alkaline earth metals are [illegible]
5. On heating in Bunsen flame, elements of both groups [illegible]

(xi) How do group 1 metals differ form group 2 metals?

1. They have one electron in their outermost s-orbital	1 They have [illegible] s-orbital
2. They have low melting points than alkaline earth metals	2 They [illegible]
3. They have relatively larger atomic size.	3 They [illegible]
4. The alkali metals are relatively softer than alkaline earth metals	4 They are [illegible]
5 They have relatively low values of ionization	5 They [illegible]

energies

6 Their oxides and ... in nature

7 They ...

$2Na + 2H_2O \rightarrow 2NaOH + H_2$ | $Mg + H_2O \rightarrow MgO + H_2$

8 Their ...

9 They ...

10 ...

11 On heating ... oxygen except Li

$2NaNO_3 \rightarrow 2NaNO_2 + O_2$

nitrogen peroxide and oxygen

$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$

(xii) Discuss the metallic and non-metallic character of group 4 elements.

The metallic character incr...

- Carbon, Silicon and ...
- "Grey tin" or "alpha tin ...
- The "white tin" or "beta ... packed arrangement ... llic bonds in a close
- Lead also shows metallic bo...

Thus a clear tr... metals

(xiii) Discuss the general group trends of group 7 elements.

- Atomic radius, melting points and boiling points increases down the group ... greater shielding effect and less nuclear change
- Electronegativity, electron affinity values decreases down the group due to increase in atomic size
- The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases down the group due to increase in atomic size except the F-F bond
- The oxidizing power decreases down the group.

(xiv) Why the term halogen is used for group 7 elements?

These form salts on reacting with metals, so they are called halogens. (Halo = salt, Gen = former)

e.g. $2Na + Cl_2 \rightarrow 2NaCl$

Other examples: KBr, NaF, LiCl, RbCl etc

(xv) Why does fluorine differ from other members of its group?

Fluorine differs from its family members due to

(i) Small size of F atom and F^- ion

(ii) High first ionization energy and electronegativity

(iii) Low dissociation energy of F_2 molecule as compared to Cl_2 and Br_2

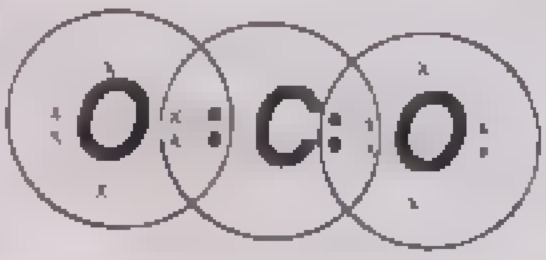
(iv) Valence shell restriction to an octet.

Differences

1. F has very small size. Thus it can from effective over... with other elements except N, O and itself. Thus it ... from shorter and stronger bonds
2. Ionic fluorides have very high lattice energies than ... halides, thus these are stable. It is due to this reason ... fluorides of Ca, Mg, Ba and Sr are insoluble in water
3. F_2 molecule has very low dissociation energy. Thus it is very reactive, other halogens react very slowly under similar conditions
4. Since valence shell of F is restricted to an ... Therefore many of its compounds show inertness ... CF_4, SF_6 etc
5. Due to restriction to an octet, F shows only -1 oxidation state, while other halogens show variable oxidation states.
6. Only F reacts with noble gases directly like Xe and Rn to give fluorides

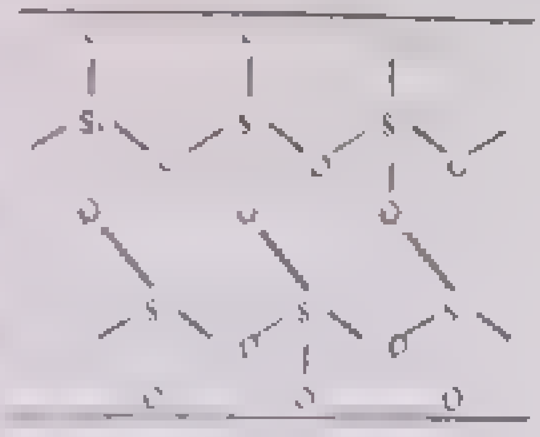
(xxi) What is the structure of CO_2 and SiO_2 and why they differ?

- The CO_2 exist in molecular form with weak intermolecular forces. Its dipole moment is zero, therefore it is a linear molecule. Due to weak forces it exists as gas at room temperature



- The SiO_2 is a macromolecular compound. In this silicon and oxygen atoms are linked together covalently in continuous chains. Thus silicon dioxide is a non-volatile and hard solid unlike carbon dioxide

The difference in structure of SiO_2 and CO_2 is due to the following two reasons



(i) Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more oxygen atoms.

(ii) Silicon from only single bond with oxygen atoms while carbon forms double bonds

(xxii) CO_2 is a gas while SiO_2 is a solid although C and Si belong to the same group?

The CO_2 exist in molecular form with weak intermolecular forces. Its dipole moment is zero, therefore it is a linear molecule. Due to weak forces it exists as gas at room temperature.

The SiO_2 is a macromolecular compound. In this silicon and oxygen atoms are linked together covalently in continuous chains. Thus, silicon dioxide is a non-volatile and hard solid.

(xxiii) Explain why nitrates and carbonates of Li are not stable?

The nitrates and carbonates of Li are decomposed on heating

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

Li has small size. So, the gain in electrostatic attraction while converting to oxide is considerable. In case of large cation like K^+, the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

(xxiv) Differentiate the behaviour of Li and Na with atmospheric oxygen

Lithium burns in atmospheric oxygen to form the normal oxide, Li_2O

$$4Li + O_2 \rightarrow 2Li_2O \text{ (Lithium oxide)}$$

Sodium burns in atmospheric oxygen to form the peroxide

$$2Na + O_2 \rightarrow Na_2O_2 \text{ (Sodium peroxide)}$$

(xxv) Alkali metal carbonates are more soluble that alkaline earth metal carbonates. Why?

The alkali metals cations have relatively larger ionic size than alkaline earth metals cations. Moreover, they have M^+ ions. Therefore, in carbonates, they have loose packing with weak forces. So their lattice energies are very low. Hence, they dissociates in water easily.

That is why alkali metal carbonates are more soluble than alkaline earth metal carbonates.

(xxvi) Explain why stability solubility of alkaline earth metal carbonates decrease down the group?

In alkaline earth metals, the ionic size increases down the group. Moreover carbonate ion is a large (large) anion. Generally, larger the size of ion, lesser is the hydration and solubility. So, due to difficulty in hydration of ions, the solubility of alkaline earth metal carbonates decreases down the group.

(xxii) Oxidizing power of F_2 is greater than I_2 Why?

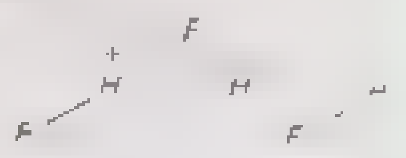
It is due to three reasons

- The bond dissociation energy of fluorine is quite low, so it will dissociate [illegible]
- The electron affinity of F is greater than I, so it will take up electron more readily
- The F^- ion has high hydration energy due to small size, so it will form readily in [illegible] main factor

It means that fluorine will take up electrons readily to form F^- [illegible] stronger oxidizing agent than iodine

(xxiii) HF is weak acid than HI Why?

In HF, molecules are Hydrongen-bonded in a zigzag manner Thus [illegible] H-atom is entrapped between two F atoms as shown in the fig



Moreover, the bond energy of H-F bond is considerably greater than H-I bond Thus, HF cannot donate its H^+ ions easily hence it is a weaker acid

(xxiv) On what factors does the oxidizing power of halogens depend?

Following factors affect oxidizing power

(a) Energy of dissociation (b) Electron affinities of atoms (c) Hydration energy [illegible]

If a halogen has low energy of dissociation, high electron affinity and high hydration energy [illegible] it will be a better oxidizing agent On the basis of these factors, the order of oxidizing power is

$$F_2 > Cl_2 > Br_2 > I_2 \text{ (weakest oxidizing agents).}$$

Q3: Give detailed answers for the following questions

(i) (a) The pattern of first ionization energy and melting and boiling point is not smooth Justify it

Ionization Energies.

In a group in periodic table, the irregularity is due to the filling of the d-orbitals and f orbitals [illegible] members of the group Since d and f-orbitals have poor shielding effect, so they cannot shield the valence electron effectively. Hence, the pattern becomes irregular.

Melting and Boiling points:

Melting and boiling points largely depends upon the structure of elements

e.g. Group 1 and 2 elements exist as metallic crystals. Thus, the melting points and boiling points of group 1 and 2 elements decrease from top to bottom due to increase in size It is because larger size atoms have weaker forces than smaller size atoms.

However, non metals of groups 7 exists as molecular substances So melting points and boiling points increase from top to bottom It is because, molecular size increases down the group. Larger molecules have greater polarizability, therefore, these have stronger intermolecular forces Thus melting points and boiling points increases down the group. Thus pattern of melting and boiling points is not smooth

(b) Why atomic radius increases in group and decreases along the period.

- The number of shells in all the elements of a given periods remains the same
- The value of effective nuclear charge, increases from left to right due to increase in number of protons
- The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right

The atomic radius increases down the group from lithium to caesium It is because, down the group number of shells increases So, the atomic volume increases Hence, atomic and ionic radii (of M^+ ions) increases from lithium to caesium.

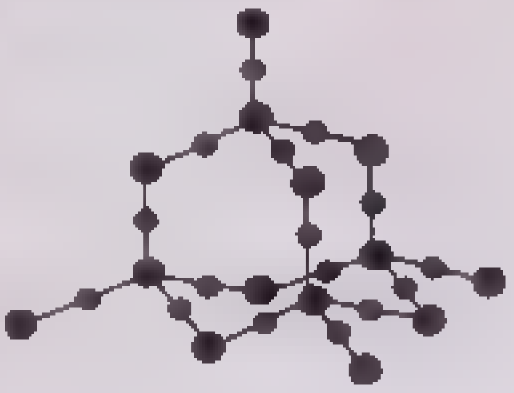
(c) Describe the trends in reaction of period 3 elements with water.
See Page 7

(d) The melting and boiling pints of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?
See Page 6

(ii) Discuss the metallic oxides and silicon dioxide under the following headings

(a) Structures

Metallic oxides. Sodium, magnesium and aluminium oxides structure diagram is same as sodium chloride



Silicon dioxide. Crystalline silicon has the same structure as diamond. In this structure atoms of both silicon and oxygen are present
In SiO_2, each silicon atom is bridged to its neighbouring silicon by an oxygen atom

(b) Melting and Boiling points

Metallic oxides and silicon dioxide have giant structures. Thus they have high melting and boiling points. It is because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions

(c) Electrical conductivity.

Metallic oxides: Metallic oxides are ionic in nature. They cannot conduct electricity in solid state because there are no free ions or electrons in solid state
However, the ionic oxides can conduct electricity in molten state. It is because free ions are present in molten state. These ions show movement towards the electrodes where they discharge themselves

Silicon dioxide. In SiO_2, all four electrons of Si are used in forming covalent bonds. Hence there are no free ions or electrons in SiO_2 so it will not conduct electricity

(iii) Discuss acid-base behaviour of

(i) Aluminium oxide

It is an amphoteric oxide. It gives reactions as both a base and an acid.
Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

(ii) Sodium oxide

It is a simple basic oxides. It reacts with water to give the sodium hydroxide

$$Na_2O + H_2O \rightarrow 2NaOH$$

It reacts with dilute hydrochloric acid to give colourless sodium chloride solution and water

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O$$

(iv) (a) Why are different types of oxides formed as you go down the group?

(b) How Beryllium differs from other members of its group?

(c) Why is Beryllium chloride covalent and not ionic?

Beryllium is more electronegative and less electropositive than its family members. So, it does not lose its electron readily. Hence, it will not form ionic bond with chlorine. It will share its electrons with chlorine to form Beryllium chloride which will be covalent in nature

(v) (a) *Why do some metals form peroxides on heating in oxygen?*

The peroxide ion has a weak covalent bond between two oxygen atoms. Small size metal ions have high charge density. So, when they come near to peroxide ion they polarize it so much that peroxide ion is broken e.g. Li^{+}, Be^{+2}, Mg^{+2} have high charge density due to smaller size so they cannot form peroxides. The metals which have larger atomic size have [illegible] so they can form peroxides e.g. Na^{+}, Ba^{+2}

(b) Why do group 2 elements form nitrides on heating in air?

To form a group 2 metal nitride energy is given for two purposes i.e. (i) to form M^{+2} ion and (ii) to break and convert nitrogen molecule into nitride ion N^{3-}. Since, M^{+2} ions are small size so they have high charge density and hence develop strong attractions for N^{3-} ion. Therefore a lot of energy is released as lattice energy. As a result the energy given to form ions is compensated by the release of energy during lattice formation. Hence, the reaction becomes energetically favourable. Therefore, group 2 elements form nitrides. Similarly Li also form nitride

(c) Discuss the trend in solubility of hydroxide of group 2 elements

The solubility of Group 2 hydroxides increases down the group as shown in [illegible]

$Be(OH)_2 = 1.6 \times 10^{-26}$ $Mg(OH)_2 = 8.9 \times 10^{-12}$
$Ca(OH)_2 = 1.3 \times 10^{-4}$ $Sr(OH)_2 = 3.2 \times 10^{-4}$ $Ba(OH)_2 = 5.4 \times 10^{-2}$

- Thus, $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble in H_2O
- The hydroxides of other metals are slightly soluble.

It is because, lattice energy decreases down the group due to increase in size

(vi) Discuss the trends in thermal stability of the carbonates and nitrates

Group 1 compounds are more stable to heat than the corresponding compounds in Group 2
The lithium compounds behave similarly to Group 2 compounds
The rest of Group 1 behave similarly but in a different way than Group 2

- The carbonates (M_2CO_3) are highly stable to heat
- With increase of electropositive character from Li to Cs, the stability of these salts increases
- Their nitrates decompose on strong heating to the corresponding nitrite and O_2

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

- The $LiNO_3$ decomposes completely to give corresponding oxide, NO_2 and O_2

$$3LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

THE EFFECT OF HEAT ON THE GROUP 2 CARBONATES

- All carbonates decompose on heating at appropriate temperature evolving CO_2

$$MCO_3 \rightarrow CO_2 + MO$$

- The values of the decomposition temperatures of these carbonates as given below

$BeCO_3 = 25°C$, $MgCO_3 = 540°C$, $CaCO_3 = 900°C$,
$SrCO_3 = 1290°C$, $BaCO_3 = 1360°C$

Thus ease of decomposition decreases down the group

THE EFFECT OF HEAT ON THE GROUP 2 NITRATES

- All nitrates of Group 2 metals undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen
- The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen

$$2M(NO_3)_{2(s)} \rightarrow 2MO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

- Magnesium and calcium nitrates normally have water of crystallisation. So, the solid may dissolve in its own water of crystallisation to make a colourless solution before it starts to decompose

(vii) Explain with examples that Beryllium hydroxide is Amphoteric?

An amphoteric oxide shows both acidic and basic properties **e.g** BeO

It reacts with acids to form salts

$$BeO + H_2SO_4 \rightarrow BeSO_4 + H_2O$$

It also reacts with bases to form salts

$$BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$$

(viii) Explain the trends in oxidation states with suitable examples

See Page 38

(ix) Discuss the inert pair effect in the:
(a) formation of ionic bonds (b) formation of covalent bonds

See Page 39

(x) Discuss in detail acid-base trend in group 4 oxides

See Page 43

(xi) Explain in detail the trends in group 7 of following physical properties
(a) Electronegativity (b) Electron affinity

See Page 45

(xii)(a) Why is the bond enthalpy of F-F less as compared to Cl-Cl and Br-Br?

- It is due to very small F-F bond length than other X-X bond lengths. So due to short distance the F atoms in F_2 molecule repel each other and thus the dissociation of F_2 molecule into F atoms becomes easy.
- X-X bond in Cl_2 and Br_2 molecules is stronger than F-F bond in F_2 molecule. It is due to the possibility of the formation of multiple bonds in X-X bond with d- orbitals.

 Hence bond enthalpy of F-F bond is less as compared to Cl [illegible]

(b) Explain the order F>Cl>Br>I with respect to oxidizing agent power

The oxidizing power of halogens depends upon dissociation energy, electron affinity and hydration energy. The net energy released from all these process decreases down the group. Thus formation of F^- ion releases most energy while formation of I^- ion releases least energy. It means that fluorine can take up electrons readily to form F^- ions. Thus, F_2 will have highest oxidizing power among halogens. Similarly I_2 [illegible] least oxidizing power among halogens.

Hence, the order of oxidizing power is $F_2 > Cl_2 > Br_2 > I_2$ *(weakest oxidizing agent)*

(xiii)(a) Why is fluorine much stronger oxidizing agent than chlorine?

It is because

- The bond dissociation energy of fluorine is quite low [illegible] rapidly to take up electron
- The other factor is hydration energy. The [illegible] energy due to small size so it will form readily in solution. Thus fluorine will take up electrons readily [illegible] form F^- ions than chlorine. Hence fluorine is a much stronger oxidizing agent than [illegible]

(b) HCl is strong acid as compared to HF. Why?

In HF molecules are Hydrogen bonded in a zig zag manner. [illegible] F atoms as shown in the fig. Moreover, the bond energy of H-F bond is [illegible]. Thus HF cannot donate its H^+ ions easily hence it is a weaker acid.

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time 25 Minutes

Note Over writing ... result in loss of marks

Marks 17

(i) *In a group the atomic radius increase due to successive increase of*
(A) electronic shells (B) proton shells (C) neutron shells (D) nuclei

(ii) *Green is characteristic flame colour of*
(A) calcium (B) barium (C) strontium (D) sodium

(iii) *The flame colour of sodium metal or its compounds is*
(A) bright crimson (B) violet (C) golden yellow (D) ...

(iv) *Due to small size of Be^{+2} ion, the oxide of BeO is*
(A) ionic (B) coordinate (C) covalent (D) none of these

(v) *Sulphur dioxide is fairly soluble in water, reacting with it to give solution of*
(A) H_2SO_4 (B) H_2SO_3 (C) H_2SO_5 (D) $NaHSO_3$

(vi) *Al_2O_3 is*
(A) Amphoteric oxide (B) Acid oxide (C) basic oxide (D) both a and b

(vii) *Peroxides of alkali metals on reaction with ice cold water produce*
(A) metal oxide (B) metal hydroxide (C) metal (D) superoxide

(viii) *Highest electron affinity is shown by*
(A) F_2 (B) I_2 (C) Br_2 (D) Cl_2

(ix) *Reducing powers of halide ions .... from I^- for Br^-*
(A) increases (B) decreases (C) remain same (D) none of these

(x) *The increasing strength of halogens as oxidizing agents is*
(A) $I_2 > Br_2 > Cl_2 > F_2$ (B) $F_2 < Cl_2 < Br_2 < I_2$ (C) $F_2 > Cl_2 > Br_2 > I_2$ (D) ...

(xi) *All the carbonates sulphates and phosphates of alkaline earth metals are ...... in water*
(A) Sparingly soluble (B) soluble (C) insoluble (D) less soluble

(xii) *Lead (II) chloride $PbCl_2$ is*
(A) white solid (B) liquid (C) volatile compound (D) both a and

(xiii) *Ge^{2+} compounds are*
(A) Reducing agents (B) Oxidizing agents (C) both a and b (D) none of these

(xiv) *Substance boiling at higher temperature among following is*
(A) HI (B) HF (C) HCl (D) HBr

(xv) *The reactivity of alkali metals generally increase from*
(A) top to bottom (B) bottom to top
(C) remain same throughout the group (D) none of these

(xvi) *The carbonates of alkali metals are not affected by heat except*
(A) Li_2CO_3 (B) Na_2CO_3 (C) K_2CO_3 (D) Rb_2CO_3

(xvii) *The radioactive element in halogen group is*
(A) Radon (B) Radium (C) Astatine (D) Bromine

Time: 2 35 Hours

SUBJECTIVE

Total Marks Section B and C 68

Section – B (Marks 42) (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

(i) Although Na and P are present in the same period yet their oxides are different in nature, Na_2O is basic while P_2O_5 acidic. Why?

(ii) (a) Write down the reaction of Mg with cold and hot water. (03)
(b) Draw the structure of ortho silicic acid (02)

(iii) Discuss the metallic and non – metallic character of group 4 elements (01)

(iv) How hydrolysis of tetrahalides takes place (03)

(v) CO2 is a gas while SiO2 is a solid although C and Si belong to the same group (03)

(vi) HF is a weak acid than HI. Why (03)

(vii) (a) Show the amphoteric nature of BeO (03)
(b) Write down the names of product formed when S_2Cl_2 react with water (02)
(01)

(viii) The oxidizing power of F is greater than Cl. Why? (03)
(ix) Discuss the general group trends of group I elements. (03)
(x) How NaoH react with H_3PO_4? (03)
(xi) Discuss the behaviour of AlCl (03)
(xii) Explain why nitrates and carbonates of Li are not stable (03)
(xiii) Differentiate the behaviour of Li and Na with amphoteric oxygen (03)
(xiv) Explain why salubility of alkaline earth metal carbonates decrease down the groups (03)
(xv) Why do the group I metals show strong electropositive character (03)
(xvi) Why normal oxides of alkali metals are not formed by the direct combination of metals with (03)
(xvii) Explain the trend of density in alkali metals (03)
(xviii) On what factors does the oxidizing power of halogen depends. (03)
(xix) Why different colours are imparted by the atoms of the group & metals to the flame (03)

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26.

Q1. Discuss the metallic oxides and silicon dioxide under the following headings
(a) Structures. (04)
(b) Melting and BoilingPoints (05)
(c) Electrical conductivity (04)

Q2. (a) Why is fluorine much stronger oxidizing agent than chlarine. (03)
(b) HCl is strong acid as compared to HF. Why
(c) Explain the trends in detail of group I
(i) Electrongtivity
(ii) Electron afficity

Q3 (a) The pattern of first ion zation energy and melting and boiling points
(b) Why atomic radius increases in group and decreases along the period
(c) Describe the trends in reaction of period 3 elements with water
(d) Why Beryllium chloride covalent and not ionic.

oxy add

Reducing agent
* reduces other substance
and loses electron;
* oxidation state
increases
* electron donor
* H_2, C, Fe, Zn, ...

Reducing agent

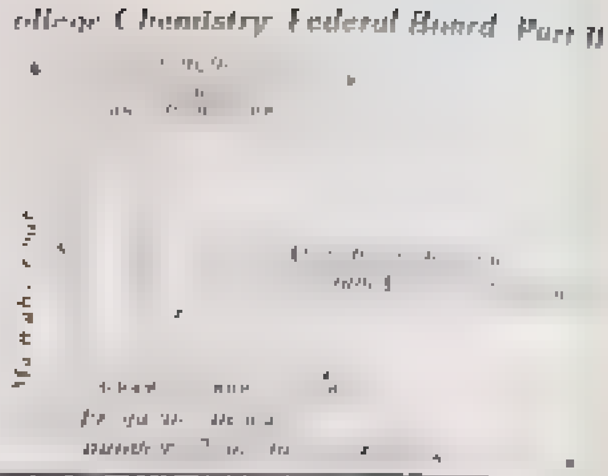
A

A losses electron

A

A is oxidized

* higher position



CHAPTER # 14

d and f-Block Elements: TRANSITION ELEMENTS

INTRODUCTION

Definition

The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements.

- They are called d-block or f block elements
- d-block elements are called outer transition elements and f-block elements are called inner transition elements

Why are they called transition elements?

- They are called transition elements because they show transition in properties between s and p block elements
- Thus there is a transition between highly reactive and strongly electropositive elements of s-block which form ionic bonds on one side and p-block elements which form covalent compounds on other side

Series of Transition Elements:

The d-block elements consist of following three series of ten elements each

(1) 3d-Series: From Scandium (Sc=21) to Zinc (Zn=30)

(2) 4d-Series: From Yttrium (Y=39) to Cadmium (Cd=48)

(3) 5d-Series. From Lanthanum (La=57) to Mercury (Hg=80) [*Lanthanide series rare earth s...*]

The f-block elements constitute two series which are

(1) 4f-Series: From Cerium (Ce = 58) to Lutetium (Lu = 71)

(2) 5f-Series: From Actinium (Ac = 89) to Lawrentium (Lr = 103) which are called actinides

General outermost configurations:

(1) d-block elements $= (n-1)d^{1-10}\ ns^2$

(2) f-block elements $= (n-1)d^1\ (n-2)f^{1-14}\ ns^2$

Remember!

The electronic configuration of $_{25}Mn$ is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$ **or** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

So, the valence subshell is ***$4s^2$ i.e. ns^2****, then d subshell is* ***$3d^5$ i.e $(n-1)d^5$****. Thus, coefficient of d subshell is one number less than the s-subshell So, the general configuration is* $(n-1)d^{1-10}\ ns^2$. The d^{1-10} means 1 to 10 electrons may be present. *Similarly, for f-block the d-subshell is one number less but the f-subshell is two numbers less than the s-subshell Thus, their general configuration is* $(n-1)d^1\ (n-2)f^{1-14}\ ns^2$

Why is Zn-group included in Transition elements?

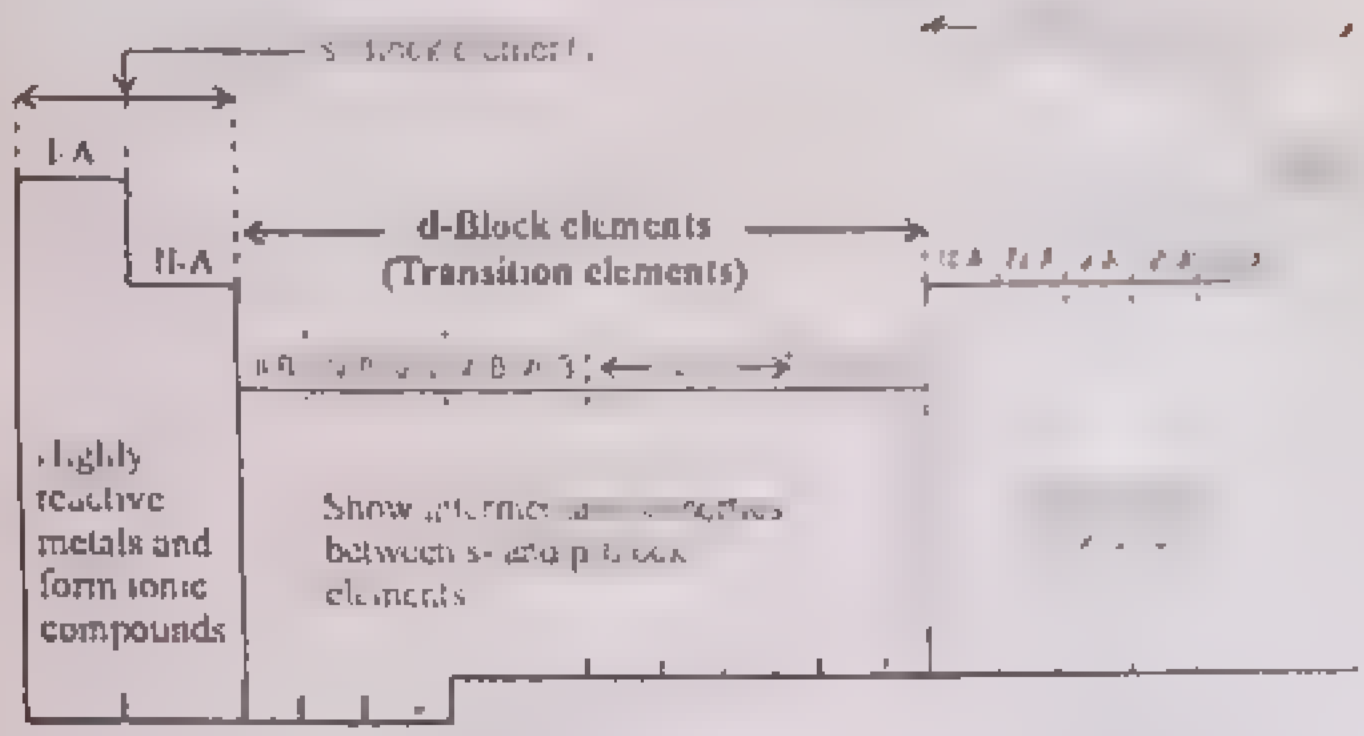
Zn, Cd and Hg are not regarded as transition elements because they have completely filled d orbitals. However they are included in transition elements because they form complexes with ammonia, halide ions and amines and their chemical behaviors is similar to transition elements.

Coinage metals are transition elements. Justify the statement.

Coinage metals are Cu, Ag, Au They are transition elements since Cu^{2+} has $3d^9$ configuration Ag^{2+} has a $4d^9$ and Au^{3+} has $5d^8$ configurations Although all these metals have d^{10} configurations in atomic states

Position of d-block elements in the periodic table

Following diagram show the position of d block e...



Position of d-block elements in the periodic table

Exercise Q3(i) (b) What are typical and non-typical transition elements?

Typical and non-Typical Transition Elements.

The elements of the group II-B and III-B have the e ectron c ...

II-B	III-B
$_{30}Zn$ = ...$4s^2 3d^{10}$	$_{21}Sc$ = $4s^2 3d^1$
$_{48}Cd$ = ...$5s^2 4d^{10}$	$_{39}Y$ = $5s^2 4d^1$
$_{80}Hg$ = ...$6s^2 5d^{10}$	$_{57}La$ = . $6s^2 5d^1$

- It is clear that the elements of II-B i.e. Zn, Cd and Hg ... state or ionic state. They do not show the typic... extent.
- The elements of the group III-B are $_{21}Sc$, $_{39}Y$ and $_{57}La$ ... transition elements. In the compound state the... they do not have any electron in d-orbita.

  For these reasons, the elements of group II-B and III-B are...

Non-Typical Transition Elements	Typical Transition Elements
II-B and III-B	

GENERAL FEATURES

GENERAL FEATURES OF TRANSITION ELEMENTS

(1) They are all metallic in nature

(2) Some of the transition elements play an important ... W, Zr, Nb, Ta and Th etc.

(3) They are all hard and strong metal with high melting ... electricity.

(4) They form alloys with one another and other elements ...

(5) With a few exceptions, they show variable oxidation states

(6) Their ions and compounds are colored in the solid state an...

QUICK QUIZ-1

(1) *Give the electronic configuration of the elements of first transition series*

First Transition series is 3d-series. It includes 1 [illegible]

(The electronic configuration is g [illegible])

(2) *Write the general state electronic configuration (s, p, d, f) of the elements of the first transition series (z=21 to 30) indicating the number of unpaired electrons in each case*

The general state electronic configuration is $(n-1)d^{1-10}ns^2$. The ind [illegible] guration of e [illegible]

Sc_{21} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Ti_{22} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

V_{23} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Cr_{24} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Mn_{25} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Fe_{26} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Co_{27} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Ni_{28} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Cu_{29} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

Zn_{30} = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$ [illegible]

(3) *Give the names, symbols and electronic configuration of the elements of second transition series*

The second transition series is 4d-series. It includes 10 elements from $_{39}Y$ to $_{48}Cd$. The electronic configuration of 4-d series elements is

4d-Series Transition Elements

Elements Symbol	Name	Electronic configuration
$_{39}Y$	Yttrium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^1$
$_{40}Zr$	Zirconium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^2$
$_{41}Nb$	Niobium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^3$
$_{42}Mo$	Molybdenum	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1\ 4d^5$
$_{43}Tc$	Technitium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^5$
$_{44}Ru$	Ruthenium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^6$
$_{45}Rh$	Rhodium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^7$
$_{46}Pd$	Palladium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^8$
$_{47}Ag$	Argentum (Silver)	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^1\ 4d^{10}$
$_{48}Cd$	Cadmium	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}$

(4) *Discuss the trends and variation in oxidation states (valency) of transition metals.*

See Page 70

(5) *Explain the magnetic properties of transition metals.*

See Page 71

(6) *What do you understand by diamagnetism and paramagnetism.*

See Page 71

[Exer]cise Q3(ii)(a): What is the valence shell configuration of transition elements? How does it affect the following properties? [illegible]

[See] this [on] page 70

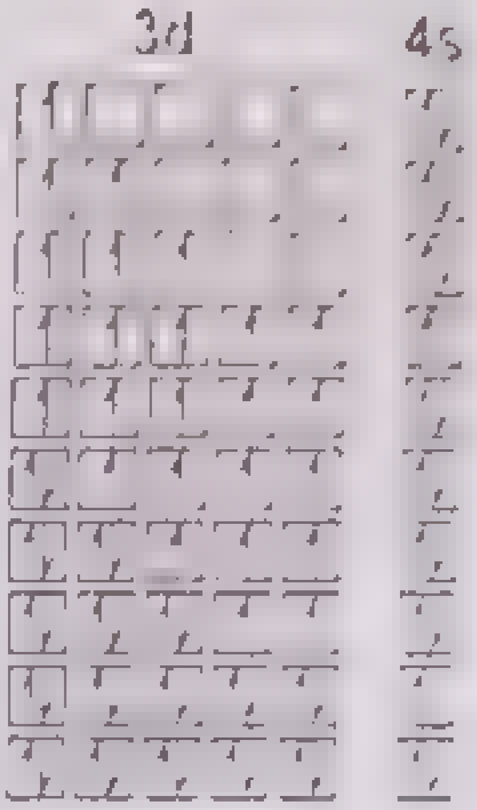
[EL]ECTRONIC STRUCTURE

Electronic distribution of first series of transition [illegible] below

- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1\ 3d^1$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ [illegible]
- [illegible] = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$ [illegible]

3d 4s

Sc (Ar)
Ti (Ar)
V (Ar)
Cr (Ar)
Mn (Ar)
Fe (Ar)
Co (Ar)
Ni (Ar)
Cu (Ar)
Zn (Ar)



[E]LECTRONIC DISTRIBUTION OF 4d AND 5d-SERIES:

- The following table shows the electronic distribution of 4d and 5d [illegible]
- The elements of the group number VI-B, i.e. Cr group shows the same [illegible]
- Similarly, the elements of the group I-B that is Cu-family also show the [illegible]
- Following table shows the electronic distribution of 3d, 4d, 5d series

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] $3d^1 4s^2$	Y (39)	[illegible]	[illegible]	[illegible]
Ti (22)	[Ar] $3d^2 4s^2$	Zr (40)	[illegible]	[illegible]	[illegible]
V (23)	[Ar] $3d^3 4s^2$	Nb (41)	[illegible]	[illegible]	[illegible]
Cr (24)	[Ar] $3d^5 4s^1$	Mo (42)	[illegible]	[illegible]	[illegible]
Mn (25)	[Ar] $3d^5 4s^2$	Tc (43)	[illegible]	[illegible]	[illegible]
Fe (26)	[Ar] $3d^6 4s^2$	Ru (44)	[illegible]	[illegible]	[illegible]
Co (27)	[Ar] $3d^7 4s^2$	Rh (45)	[illegible]	[illegible]	[illegible]
Ni (28)	[Ar] $3d^8 4s^2$	Pd (46)	[illegible]	[illegible]	[illegible]
Cu (29)	[Ar] $3d^{10} 4s^1$	Ag (47)	[illegible]	[illegible]	[illegible]
Zn (30)	[Ar] $3d^{10} 4s^2$	Cd (48)	[illegible]	[illegible]	[illegible]

Exercise Q3(i)(a) *What is the valence shell configuration of transition elements? How does it affect the following properties? (i) Binding energy (ii) Paramagnetism (iii) oxidation states*

For this see above page 69

BINDING ENERGY

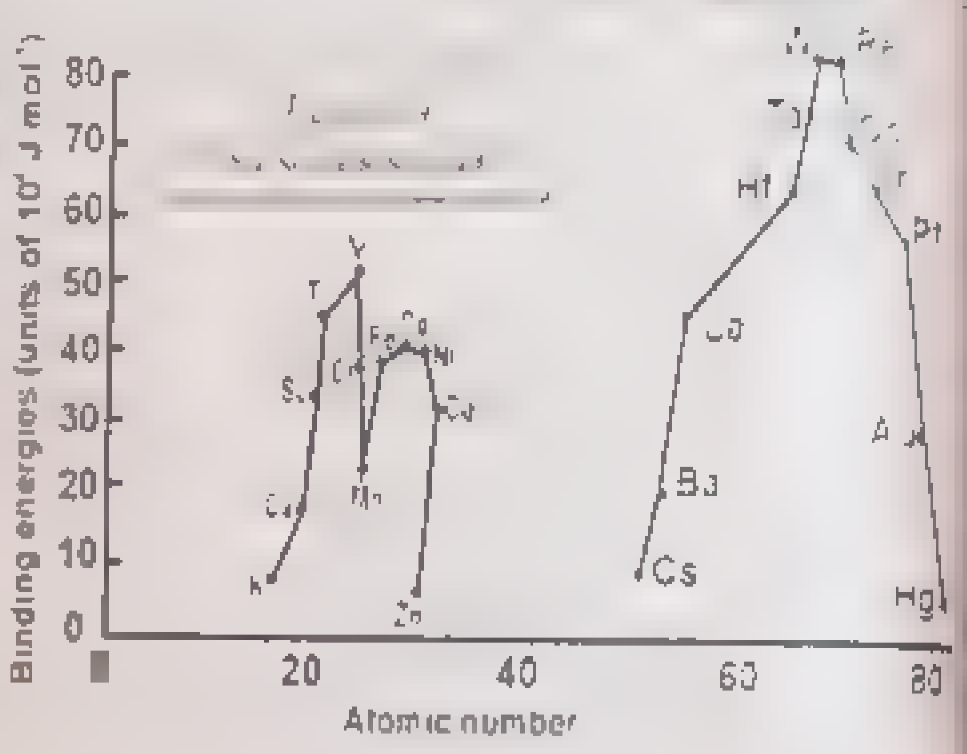
- The mechanical properties of transition elements are related with the binding energy.
- Transition elements are tough, malleable and ductile

The toughness of the metals is due to greater binding energies

It is because the s-electron of outermost shell takes part in chemical bonding. However, the electrons of partially filled d-orbitals also participate in bonding. So, they have greater binding energies and toughness

Variation in binding energies:

- The number of unpaired electrons increases up to group V-B from left to the right in any d-block series. i.e., up to V family (group V-B or group 5) or Cr family (group VI-B or group 6)
- After that the pairing of electron starts
- The unpaired electrons become zero at **group** II-B
- It means that binding forces go on increasing up to Cr and then decrease after that. This is shown for the elements of 3d and 5d series in the figure



Quick Quiz-1 (4): Discuss the trends and variation in oxidation states (valency) of transition metals

VARIABLE OXIDATION STATES

- Transition elements are electropositive, so they have positive oxidation states
- All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding
- ***Transition elements show variable oxidation states.*** The reason is that they have d-electrons in addition to s-electron for bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons
- In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.
- Among the 3d series, Mn has maximum oxidation states, and goes up to +7.
- The oxidation numbers +2 and +3 are more common.
- ***Positive oxidation states increase up to the middle of series and after that they decrease.*** It is because the number of unpaired electrons increases up to the middle and then decreases

			3d	4s	Oxidation states
Sc	[Ar]	$3d^1 4s^2$	↑	↑↓	2 3
Ti	[Ar]	$3d^2 4s^2$	↑ ↑	↑↓	2 3 4
V	[Ar]	$3d^3 4s^2$	↑ ↑ ↑	↑↓	2 3 4 5
Cr	[Ar]	$3d^5 4s^1$	↑ ↑ ↑ ↑ ↑	↑	2 3 4 5 6
Mn	[Ar]	$3d^5 4s^2$	↑ ↑ ↑ ↑ ↑	↑↓	1 2 3 4 5 6 7
Fe	[Ar]	$3d^6 4s^2$	↑↓ ↑ ↑ ↑ ↑	↑↓	1 2 3 4 5 6
Co	[Ar]	$3d^7 4s^2$	↑↓ ↑↓ ↑ ↑ ↑	↑↓	2 3 4 5
Ni	[Ar]	$3d^8 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	2 3 4
Cu	[Ar]	$3d^{10} 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	1 2 3
Zn	[Ar]	$3d^{10} 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	2

Quiz-1 (5): *Explain the magnetic properties of transition metals*

Quiz-1 (6): *What do you understand by diamagnetism and paramagnetism*

MAGNETIC BEHAVIOUR

Paramagnetism

The compounds attracted into the magnetic field are called paramagnetic and the phenomenon is called paramagnetism

Examples: Mn^{+2}, Fe^{+2} etc

Diamagnetism

The compounds which are slightly repelled by magnetic field are called diamagnetic and the phenomenon is called diamagnetism.

Some substances in which even number ...

Examples: Zn^{+2}, Sc^{+3} etc

Ferromagnetism

The substances which can be magnetized are called ferromagnetic and the phenomenon is called ferromagnetism.

e.g. Fe, Co and Ni are ferromagnetic

Magnetic moment

The magnetic moment (μ) is related to the number of unpaired ...

$\mu = \sqrt{n(n+2)}$, where n = number of unpaired electrons ...

It is measured in Bohr magneton. Its symbol is μ_B

By measuring magnetic moment, the nature of transition met... metal can be calculated

Exercise Q3(i) (c) *Explain catalytic Activity of transition elements*

CATALYTIC ACTIVITY

Most of the transition elements are used as catalysts. The compounds of transition ... ***catalysts.***

It is due to following reasons

- The reason is that the transition metals show variety of oxidation states ... products with various reactants
- They also form interstitial compounds which can absorb an activator ...

Some of the important examples of catalysts are as follows

(1) A mixture of **ZnO and Cr_2O_3** is used for the manufacture of methyl a...

(2) **Ni**, **Pt** and **Pd** are catalysts for the hydrogenation of vegetable oil and ... alkenes

(3) **MnO_2** can be used as a catalyst for the decomposition of H_2O_2

(4) **$TiCl_4$** is used as catalyst for the manufacture of plastics

(5) **V_2O_5** is used to oxidize SO_2 to SO_3 in the manufacture of H_2SO_4

(6) **Fe** is used as a catalyst for synthesis of NH_3 in Haber's process about 1% of Na_2O or K_2O and about 1% ... or Al_2O_3 are added as promotors. **Mo** is also sometimes used as a promoter

ALLOY FORMATION

- Alloy is mixture of two or mo[illegible]
- ***Transition metals form alloys with each other*** [illegible] atoms [illegible] metal [illegible] alloys among them [illegible]

Example.

(1) Alloy stee[illegible] properties than iron

(2) Brass, bronze and coinage alloys are the best alloys.

Properties:

As alloys are prepared [illegible]
However, few properties are common [illegible]

(1) Alloys are comparatively cheap
(2) They are strong and flexible but hard alloys can also be prepared
(3) They have long life because they do not corrode
(4) They are durable
(5) They have high melting points
(6) They are better conductor but non-conductor alloys are also prepared

Exercise Q3(i) (d) Write composition, properties and uses of Brass, Bronze and Nichrome alloys

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 – 80 % Zn = 20 – 40 %	• It is a strong alloy of copper which is soft and flexible • It does not corrode • Due to low melting point, it is easy to use • It is used to make locks, keys, water taps, pipes, artic[illegible] door handles and parts of machines
Bronze	Cu = 90 - 95 % Sn = 5 - 10 %	• It is strong, brilliant and long lasting. • It does not corrode. • It is used to prepare medals, coins, badges and bullets etc • Besides these, decorative articles are also made from this alloy
Nichrome		It is used in electric heaters and filaments of furnaces

QUICK QUIZ-2:

(1) How magnetic moment is measured

- Theoretically, the magnetic moment (μ) is related to the number of unpaired electrons (n) by the equation

  $\mu = \sqrt{n(n+2)}$, where n = number of unpaired electrons in a substance
- Experimentally, the magnetic moment of compounds is generally measured by Guoy balance method

(2) Give unit of magnetic moment

The magnetic moment is measured in the units of Bohr Magneton. Its symbol is μ_B

(3) Give difference between nichrome and bronze

Both these are alloys.
The nichrome alloy consists of Ni = 60 %, Cr = 15 % and Fe = 25 %
The Bornze alloy consists of Cu = 90 - 95 % and Sn = 5 - 10 %.

Q. Name the catalyst use for

(i) Decomposition of H_2O_2

Manganese(IV) oxide MnO_2

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O$$

(ii) Manufacturing of CH_3OH

A ...

$$CO + 2H_2 \xrightarrow[450\text{-}500^\circ C]{ZnO/Cr_2O_3} CH_3OH$$

Q. On which factor binding energy depends

The binding energy ... unpaired electrons ... e.g. ... electrons increases up to the ... middle and then decreases ...

Q. Why transition element shows variable oxidation states

They show variable oxidation ... formation. These elements have several ... very close to each other ... oxidation states

Q. Which property of transition elements enable them to serve as catalyst

It is due to following reasons

- The reason is that the transition metals show ... intermediate products with various reactants
- They also form interstitial compounds which can absorb ...

Q. Why alloys are prepared?

Alloys are prepared due to several desirable properties e.g.

(i) Alloys are comparatively cheap

(ii) They are strong and flexible but hard alloys can also be prepared

(iii) They have long life because they do not corrode

(iv) They have high melting points

COORDINATION COMPOUNDS

Definition:

Those compounds which contain complex molecules or complex ions capable of independent existence are called coordination compounds or complex compounds.

Such compounds are formed by the coordination of an electron pair donor to metal atom or ion.

Explanation.

- Let two substances are mixed together, i.e., KCN and $Fe(CN)_2$
- When this mixture is evaporated, a new compound is obtained
- This compound when dissolved in water ionizes into K^+ and $[Fe(CN)_6]^{-4}$
- On this basis the new compounds has been given the formula $K_4[Fe(CN)_6]$

$$4KCN + Fe(CN)_2 \rightarrow K_4[Fe(CN)_6]$$

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

$[Fe(CN)_6]^{-4}$ is called complex ion.

PARTS OF COMPLEX COMPOUND AFTER DISSOCIATION IN A SOLVENT

A complex compound is mostly made up of ...

(1) Positively ch...

(2) Negati... charged

e.g. in $K_4Fe(CN)_6$, K^+ is a ca...

Complex Ion as Cation.

In some of the complexes, the positively charged ion is complex ion

$$[Cu(NH_3)_4]SO_4 \rightarrow [Cu(NH_3)_4]^{+2} + SO_4^{-2}$$

Complex Ion as Anion

In some of the complexes the negatively charged ion is the complex ion

$$K_4Fe(CN)_6 \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

COMPONENTS OF COMPLEX COMPOUNDS

Complex compound consist of three components

1. A positively or negatively charged ion which is not complex
2. A central metal atom or ion which is consisted of transition element
3. Electron pair donor which is negatively charged, positively charged or neutral

(A) CENTRAL METAL ATOM OR ION

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands

Examples:

(1) In $K_4[Fe(CN)_6]$, Fe^{+2} is the central metal ion. Six ligands (CN^- ions) are surrounding it

(2) In $K_3[Fe(CN)_6]$, Fe^{+3} is the central metal ion. Six ligands (CN^- ions) are surrounding it

(3) In $[Cu(NH_3)_4]SO_4$, Cu^{+2} is the central metal ion. Four ligands (NH_3 ions) are surrounding it

(4) In $[Ag(NH_3)_2]Cl$, Ag^{+2} is the central metal ion. Two ligands (NH_3) are surrounding it

Exercise Q3(ii) (a) Explain different types of ligand with examples

(B) LIGAND

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples:

(1) In $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, CN^- is the ligand.

(2) In $[Cu(NH_3)_4]SO_4$ and $[Ag(NH_3)_2]$ Cl, NH_3 is the ligand

TYPES OF LIGANDS.

Depending upon number of donatable electron pairs, ligands are of many types.

(1) ***Monodentate Ligands:***

Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral

Examples:

(1) Negatively charged ligands F^-, Cl^-, Br^-, I^-, OH^-, CN^-

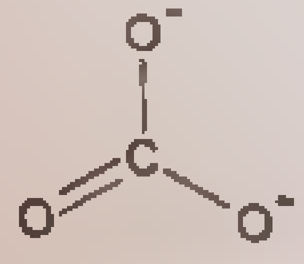
(2) Neutral ligands H_2O, NH_3, CO

(2) **Bidentate ligands.**

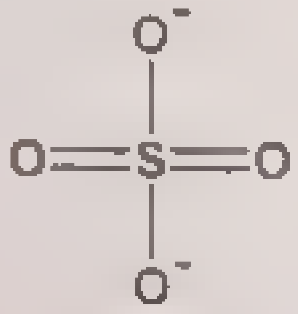
Those ligands which have two donatable electron pairs [illegible]

Examples

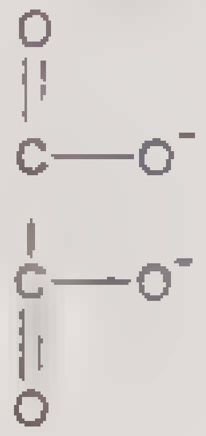
CO_3^{-2}, Carbonate ion, SO_4^{-2}, Sulphate ion, $(COO)_2^{-2}$, NH_2-NH_2, NH_2-CH_2-CH_2-NH_2



carbonate ion



sulphate ion



oxalate ion

(3) **Tridentate ligands.**

Those ligands which have three donatable electron pairs

Example:

$H_2\ddot{N} - CH_2 - CH_2 - \ddot{N}H - CH_2 - CH_2 - \ddot{N}H_2$

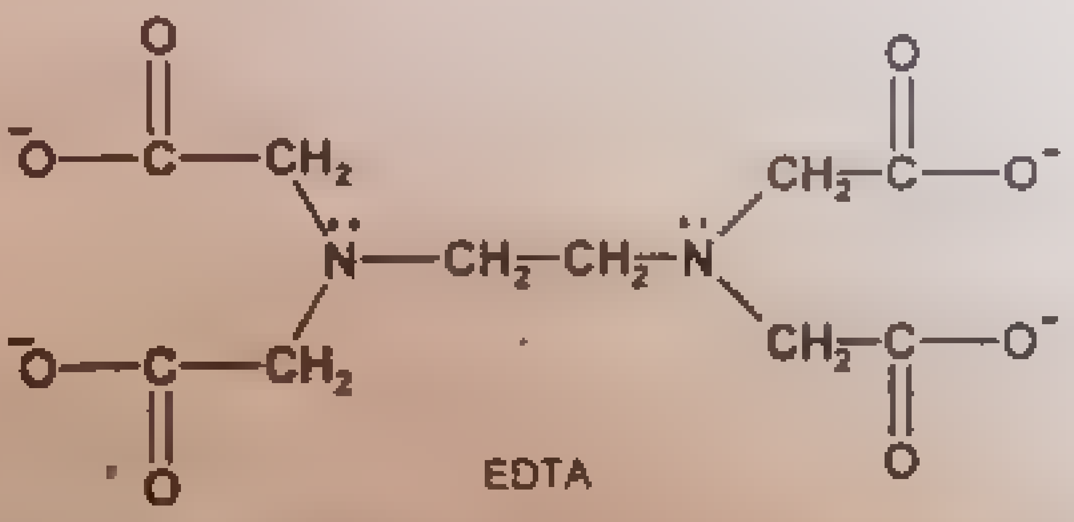
Diethylene triammine

(4) **Hexadentate ligands:**

Those ligands which have six donatable electron pairs

Example:

Ethylenediamenetetracetate (EDTA)



EDTA

COORDINATION NUMBER OR LIGANCY:

It is the total number of the atoms of the ligands that can coordinate to the central metal ion. Numerically, coordination number represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands.

Examples:

(1) In $K_4[Fe(CN)_6]$, the coordination number of Fe^{+2} is six.

(2) In $[Cu(NH_3)_4]SO_4$, the coordination number of Cu^{+2} is four

(3) In $[Ag(NH_3)_2]$, the coordination number of Ag^+ is two

(4) In $[Ni(CO)_4]$, the coordination number of Ni^0 is four

(D) COORDINATION SPHERE

The central neutral atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples:

(1) In $K_4[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-4}$ is the coordination sphere of this complex c...

(2) In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{+2}$ is the coordination sphere of this com...

(3) In $K_3[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-3}$ is the coordination sphere of this complex com...

(4) In $[Ag(NH_3)_2]Cl$, the ion $[Ag(NH_3)_2]^{+1}$ is the coordin...

(5) In $[Ni(CO)_4]$, the ion $[Ni(CO)_4]$ is the coordination...

(E) CHARGE ON THE COORDINATION SPHERE

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands

Example:

In $K_4[Fe(CN)_6]$ the charge on the coordination sphere can be calculated as follows

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{-4}$$

Since charge on each ligand is	$= -1$
Charge on $6CN^-$	$= -6$
Charge on iron	$= +2$
So the charge on the coordination sphere	$= -6+2 = -4$

NOMENCLATURE OF COMPLEX COMPOUNDS

Exercise Q3(ii) (b) Describe the rules for naming the coordination complexes with examples

Complex compounds are named according to following rules give by IUPAC

(1) Order of Ions.

Cations are named first and then the anions.

Examples:

In $K_4[Fe(CN)_6]$, we will call K^+ first and then $[Fe(CN)_6]^{-4}$

In $[Cu(NH_3)_4]SO_4$, we will call $[Cu(NH_3)_4]^{+2}$ first and then SO_4^{-2}

(2) Naming of ligands:

(i) The ligands which are negatively charged end in O e.g.

Ligand	Name	Ligand	Name
F^-	Fluoro	CN^-	Cyno
Cl^-	Chloro	CH_3COO^-	Acetato
Br^-	Bromo	$C_2O_4^{-2}$	Oxalato
I^-	Iodo		

(ii) Neutral ligands are called as such. e.g.

Ligand	Name	Ligand	Name
H_2O	Aquo or Aqua	CO	Carbonyl
NH_3	Ammine	NO	Nitrosyl

(iii) Positively charged ligands end in 'ium' e.g.

Ligand	Name	Ligand	Name
$NH_2NH_3^+$	Hydrazinium	NH_4^+	[illegible]
NO^+	Nitr[illegible]		

Order of ligands

All ligands are arranged a[illegible] not considered

More than one same type of ligands

The prefixes di for two, tri for three [illegible] more than one ligands use [illegible]

Termination of name of metal

If the complex ion is negatively [illegible]

e.g. In $K_4[Fe(CN)_6]$, the name is [illegible]

Oxidation number of metal ion

The oxidation number of the meta[illegible] of the metal

More than one polydentate ligands

The number of polydentate ligands is indicated by bis for tw[illegible]

Examples:

(a) In the following complexes, the complex ion has negative charge. So, the name of the metal ends in ate.

(1) $K_4[Fe(CN)_6]$	Potassium hexacyanoferrate (I[illegible]
(2) $K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III[illegible]
(3) $Na[Mn(CO)_5]$	Sodium Pentacarbonylmanganate [illegible]
(4) $K_2[PtCl_6]$	Potassium hexachloroplatinate (IV[illegible]
(5) $Na_2[Ni(CN)_4]$	Sodium tetracyanonickelate
(6) $Na_2[Fe(CN)_5NO]$	Sodium pentacyanonitrosylferrate(III
(7) $(NH_4)_2[PtCl_6]$	Ammonium hexachloroplatinate(IV)
(8) $K_3[Cu(CN)_4]$	Potassium tetracyanocuprate(II)
(9) $[Co(H_2O)_6]^{2+}$	Hexaaquocobalt(II) ion
(10) $[Fe(H_2O)_6]^{2+}$	Hexaquoiron(II) ion
(11) $Na_3[CoF_6]$	Sodium hexafluorocobaltate(III)

(b) In the following complexes the complex ion has positive charge. So the name of the metal is called as such:

(1) $[Co(NH_3)_6]Cl_3$	Hexaamminecobalt (III) chloride
(2) $[Co(F)_6]Cl_3$	Hexafluorocobalt (III) chloride
(3) $[Cr(H_2O)_6]Cl_3$	Hexaaquochromium (III) chloride
(4) $[Co(en)_2Cl_2]Cl$	Dichlorobisethylendiamminecoblat (III) chl[illegible]
(5) $[PtCl(NO_2)(NH_3)_4]SO_4$	Tetraamminechloronitro platinum (IV) sulphate

> ***"en"*** is the abbrevia[illegible]
> ***"ethylene diammine"***
> *The formula is*
> $H_2N-CH_2-CH_2-NH_2$

(7) $[Ag(NH_3)_2]Cl$ Diamminesilver(I) chloride
(8) $[Co(NH_3)_6]Cl_3$ Hexaamminecobalt(III) chloride
(9) $[CrCl_2(H_2O)_4]Cl$ Tetraaquadichlorochromium(III) chloride
(10) $[Ni(CN)_4]^{2-}$ Tetracyanonicklate(II) ion

(c) ***The following complexes are neutral. Therefore, they have ONE WORD name***

(1) $[Ni(CO)_4]$ Tetracarbonylnickle(0)
(2) $[Co(NH_3)_3(NO_2)_3]$ Triamminetrinitrocobalt(III)
(3) $[Fe(CO)_5]$ Pentacarbonyliron(0)

SHAPES OF COMPLEX IONS WITH COORDINATION NUMBER 2, 4 AND 6

Exercise Q3(iii) (a) Explain shapes and origin of colors of coordination compounds

- The coordination number shown by metals in complexes are 2 to 9
- The most common are 2, 3 and 6.
- Geometries corresponding to C.N's =2, 3, 4 and 5 are shown in Fig. 14 3

(1) Coordination Number 2

The complexes having C N=2 are linear, since this geometry provides minimum ligand ...
Cu^+, Ag^+ and in some cases Hg^{+2} form such complexes.

Examples:

$Cu(CN)_2$, $Cu(NH_3)_2^+$, $Ag(NH_3)_2^+$, $Ag(CN)_2^-$, $Au(CN)_2^-$, ...

(2) Coordination Number 4

Complexes with CN=4 may be tetrahedral or square planar in geometry

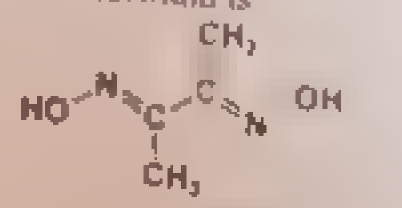
Examples of tetrahedral geometry:

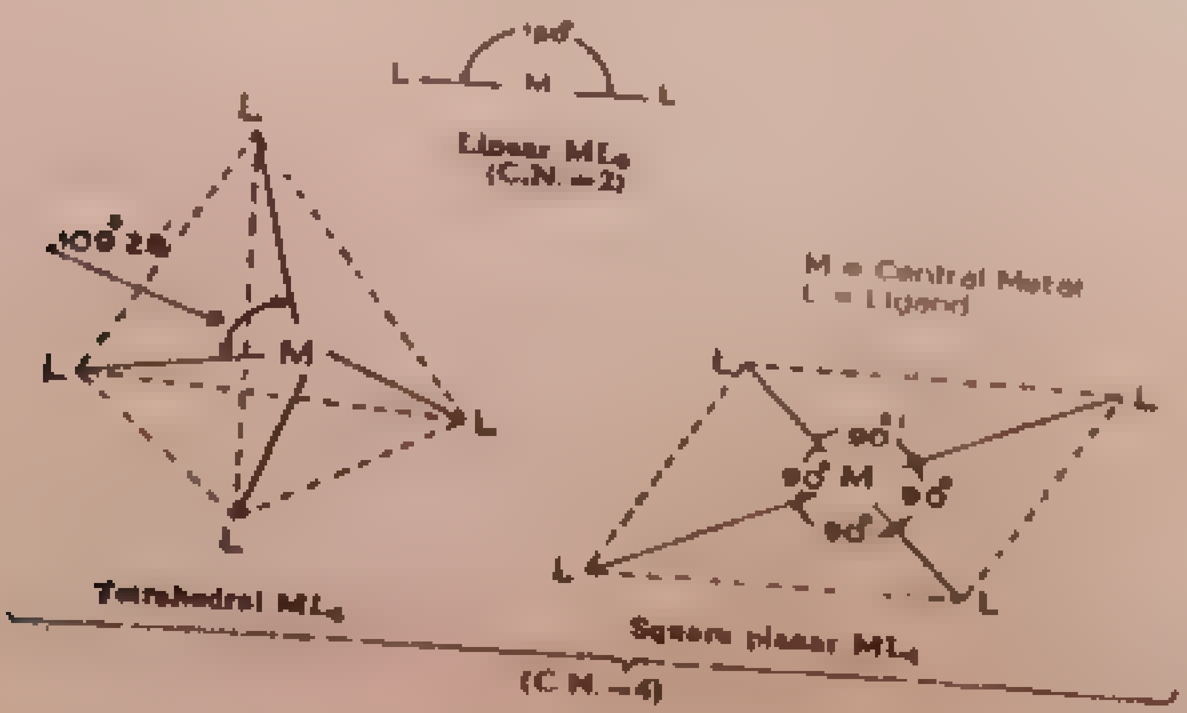
$ZnCl_4^{2-}$, $Cu(CN)_4^{2-}$, $Hg(CN)_4^{2-}$, $[Ni(CO)_4]^0$, $FeCl_4^-$, $ZnBr_4^{2-}$, $Zn(CN)_4^{2-}$ ...
CuX_4^{2-} (X = Cl, Br, CNS)
Oxyanions such as VO_4^{3-}, CrO_4^{2-}, FeO_4^{2-} and MnO_4^- are also tetrahedral

Examples of square planar geometry are found with Cu^{2+}, Ni^{2+}, Pt^{2+}, Pd^{2+}, Au^{3+} etc ions

$Ni(NH_3)_4^{2+}$, $Ni(CN)_4^{2-}$, $[Ni(dmg)_2]^0$, $Pt(NH_3)_4^{2+}$,
$PdCl_4^{2-}$, $AuCl_4^-$, $[Cu(en)_2]^{2+}$, $Cu(NH_3)^{2+}$ etc

"dmg" is the abbr...
"Dimethyl glyoxime"
The formula is

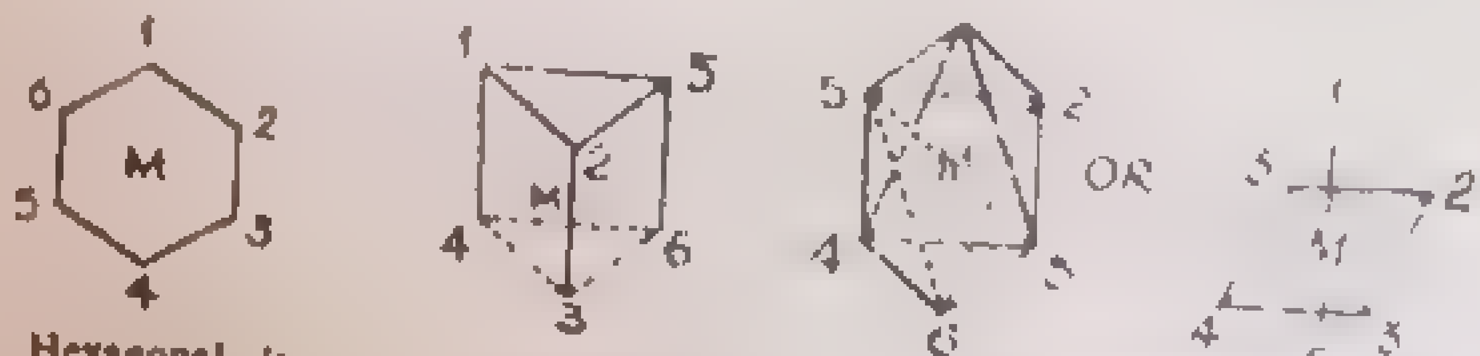




Coordination Number 6

Complexes with C.N = 6 are the most common [illegible]

- Six ligands in a 6-coordination compound [illegible] the central metal ion, M, in following ways:
  - ✓ at the corners of hexagonal planar [illegible]
  - ✓ at the apices of a trigonal prism [illegible]
  - ✓ at the apices of a regular octahedron [illegible]
- These arrangements are shown in the [illegible]
- An extensive study of the [illegible] arrangement of six ligands in a [illegible]
- The discussions of other possible [illegible] historical interest only.



Hexagonal planar geometry

Trigonal prismatic geometry

Regular octahedral geometry

COLOR OF COMPLEXES

- When white light is allowed to fall on a complex. The following [illegible]
  - *(i)* The complex may absorb the whole of white light [illegible]
  - *(ii)* The complex may reflect or transmit the whole light [illegible]
  - *(iii)* The complex may absorb some of it and may reflect [illegible] complex has some color. i.e it is colored.
- The absorption of light by the colored complexes takes place in the [illegible] extends from 4000Å to 7000Å in wavelengths.
- The color of the absorbed light is different from that of the transmitted [illegible] of the absorbed and reflected light is shown in fig below.
- The color of the transmitted light is called the complementary color of [illegible] the actual color of the complex.

Thus

(i) Hydrated cupric sulphate containing $[Cu(H_2O)_4]^{2+}SO_4^{2-}$ ions is blue because [illegible]

(ii) Cupric ammonium sulphate containing $[Cu(NH_3)_4]^{2+}$ ions is violet because [illegible]

(iii) $[Ti(H_2O)_6]^{3+}$ is purple because it absorbs green light.

The complex ions which absorb light in the infrared or ultraviolet regions of the spectrum are [illegible]

Examples:

(i) anhydrous cupric sulphate is colorless since it absorbs light in the infrared region

(ii) $[Cu(CN)_4]^{4-}$ ion is colorless since absorbs light in the ultraviolet region

Higher ——— Decreasing Energy ———→ Low

Colour absorbed	Violet	Blue	Green-blue	Blue-green	Green	Yellow-green	Yellow	Orange	Red
Colour transmitted (observed or reflected) which is the colour of the complex	Yellow green	Yellow	Orange	Red	Purple	Violet	Blue	Green	Blue Green

Wave length of the absorbed light: 4000 Å 4350 4800 4900 5000 5600 5800 5900 6050 7000

Low ——— Increasing wavelength ———→ High

Application of absorption spectrum to determine the colour of the complex

With the help of visible absorption spectrum of a complex ion it is possible to predict the color of the complex

Example:

$[Ti(H_2O)_6]^{3+}$ ion shows absorption maxima at a wavelength of about 5000Å which is equal to the wave number $\bar{\nu} = 20000\ cm^{-1}$

It can be calculated as

Wavelength = λ = 5000Å = 5000×10^{-8} cm *(Since 1Å = 10^{-10} m = 10^{-8} cm)*

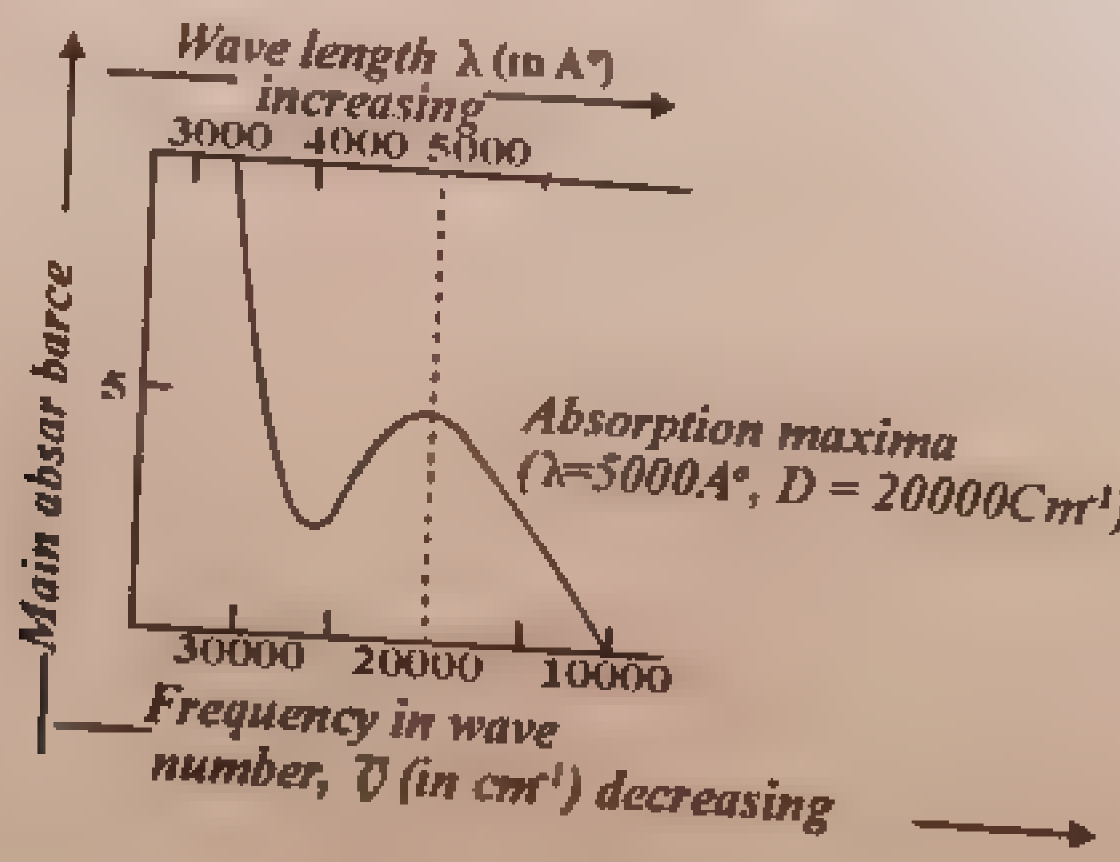
Thus

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5000 \times 10^{-8}}$$

$$= 0.2 \times 10^{5} cm^{-1} = 20000\ cm^{-1}$$

Light of this wave length (5000Å) is green and is absorbed by the complex ion

Thus the transmitted light is purple, which is in fact, the color of the ions



QUICK QUIZ-3

1. **Why do most of the transition metal ions possess a distinctive color?**

Molecular Level Explanation

e.g. $[Ti(H_2O)_6]^{3+}$

2. **What is wavelength of green color**

   It is in the range of 500

3. **When complex compound appear black**

   The complex may absorb

4. **What will be geometry of complex compound having**

   See Page 78

5. **Give examples of hexadentate and tridentate ligand**

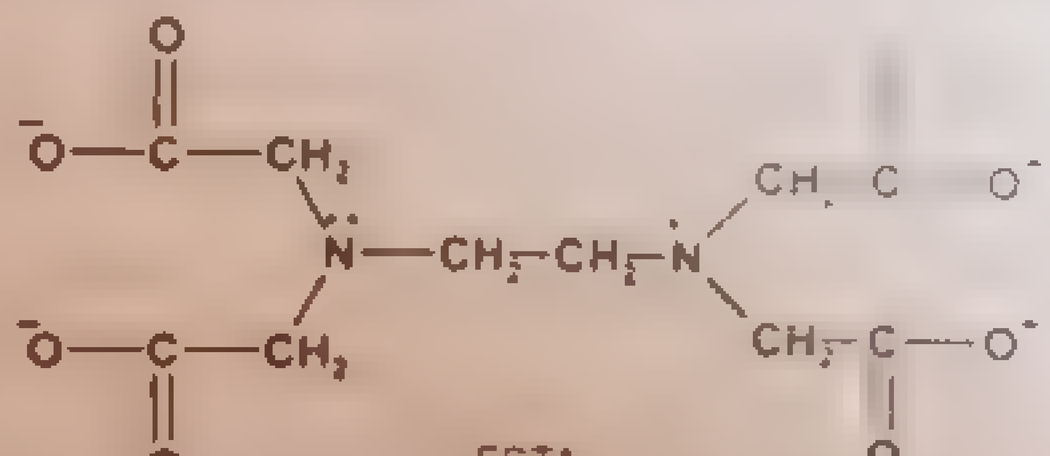
   Those ligands which have three donatable electron pairs

   Example: Diethylene triammine

   $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$

   Those ligands which have six donatable electron pairs

   Example: Ethylenediaminetetracetate (EDTA)



EDTA

CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

VANADIUM

Vanadium is important because of

(i) The conversion between various Vanadium Oxidation states and

(ii) The use of Vanadium (V) oxide as a catalyst in the contact process

VANADIUM'S OXIDATION STATES

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. These can be inter converted. It can be explained in terms of standard redox potentials (standard electrode potentials)

OBSERVING THE CHANGES IN THE LAB

REDUCING VANADIUM (V) IN STAGES TO VANADIUM (II)

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate

- It is not very soluble in water. Therefore, it is usually first dissolved in sodium hydroxide solution
- The solution can be reduced using zinc and an acid (HCl or H_2SO_4)
- The acids used are usually moderately concentrated acid.
- The exact vanadium ion present in the solution is very complicated, and varies with the pH of the solution
- The reaction is done under acidic conditions when the main ion present is VO_2^+. It is called the dioxovanadium (V) ion
- *The reduction from +5 to +4 is shown in the figure*

Note: *The ion is usually written as VO_2^+ but is more accurately $[VO_2(H_2O)_4]^+$*

Oxidation state = +5

VO_2^+

Yellow

This isn't a new oxidation state. The green is a mixture of the original yellow and the blue that is being produced

Green

Oxidation state = +4

VO^{2+}

Blue

It is important to notice that the green colour produced is not actually another oxidation state. It is just a mixture of the original yellow of the +5 state and the blue of the +4

Do you know?

Just like the VO_2^+ ion, the VO^{2+} ion will have water molecules attached to it as well $[VO(H_2O)_5]^{2+}$. We usually use the simpler form

- The reduction of V(IV) further continue and the colour changes also continue

Oxidation state = +4

VO^{2+}

Blue

Oxidation state = +3

"$V(H_2O)_6^{3+}$"

Green

Oxidation state = +2

$V(H_2O)_6^{2+}$

Purple

- The vanadium (III) ion is shown in inverted commas. It is because this formula is a simplification only. The exact nature of the complex ion will depend on the type of acid used in the reduction process

OXIDATION OF THE VANADIUM (II)

- The vanadium (II) ion is very easily oxidized
- If cotton wool is removed from the flask
  of its contact with oxygen in the air. Thus
- If it is allowed to stand for a long time
  vanadium (IV) state i.e., VO^{2+} ions.
- Nitric acid is a powerful oxidizing agent
  blue VO^{2+} ions. Thus vanadium (II) is
  The vanadium(II) oxidation state is easily

OXIDATION BY HYDROGEN IONS

- The original reduction was carried out using
  wool to keep the air out because a
- The hydrogen ions present in the solution can
- The vanadium (II) solution is only stable as
  The zinc is necessary to keep the vanadium reduced

Oxidation of Vanadium (II) to Vanadium (III)

Let H^+ ions are present and zinc is not there. The reduction potentials

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^0 = -0.26\ V$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^0 = 0\ V$$

Since,

- The reaction with the more negative E° value goes to the left (or
- The reaction with the more positive value (or less negative value

Therefore,

- The vanadium (II) ions will be oxidized to vanadium (III) ions (i.e. the
- The hydrogen ions will be reduced to hydrogen (i.e., the reaction goes to

Oxidation of Vanadium (III) to Vanadium (IV)

The E° values are

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \qquad E^0 = +0.34\ V$$

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \qquad E^0 = 0\ V$$

- In order for the vanadium equilibrium to move to the left, it should have the more negative
- However, it has not got the more negative E° value than hydrogen. Hence the reaction will not occur

OXIDATION BY NITRIC ACID

Oxidation of Vanadium (II) to Vanadium (III)

Consider the reduction potentials

$$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^0 = -0.26\ v$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \qquad E^0 = +0.96\ v$$

- The vanadium reaction has the more negative E° value and so will move to the left
- The nitric acid reaction moves to the right.
- Hence, nitric acid will oxidize vanadium (II) to vanadium (III).

Oxidation of Vanadium (III) to Vanadium (IV)

Consider the reduction potentials

$$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)} \quad E^o = +0.34\ V$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \quad E^o = +0.96\ v$$

- The nitric acid again has the more positive E° value and so m... right
- The more negative (less positive) vanadium reaction moves to the left
- Hence, nitric acid will oxidize vanadium (III) to vanadium (IV

Oxidation of Vanadium (IV) to Vanadium (V)

Consider the reduction potentials

$$VO_2^{+}{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}{}_{(aq)} + H_2O_{(l)} \quad E^o = +0.34\ V$$

$$NO_3^-{}_{(aq)} + 4H^+_{(aq)} + 3e^- \rightleftharpoons NO_{(g)} + 2H_2O_{(l)} \quad E^o = +0.96\ v$$

- If the vanadium reaction to move to the left towards dioxovanad...m (V) ion ... should have the more negative (less positive) E° value.
- However, it has not got a less positive value (or more negative value. Thus the reaction will not occur.

Other oxidizing agents can be analyzed in a similar way

Conclusions:

- If E° values show that a reaction is *possible*, then it should not be assumed that it will necessarily occur
- Practically the reaction can be too slow due to high activation energy. Therefore it may not actually happen

Exercise Q3(v) (a) Discuss vanadium (V) oxide as a catalyst with example.
Quick Quiz-4 (4). How V_2O_5 use as catalyst for oxidation of $SO_2\ (g) \rightarrow SO_3\ (g)$

VANADIUM (V) OXIDE AS A CATALYST IN THE CONTACT PROCESS

The overall reaction

During the Contact Process for manufacturing sulphuric acid, sulphur dioxide has to be converted into Sulphur trioxide

This is done by passing Sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst

$$SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

How the reaction works

- The transition metals and their compounds have ability to act as catalysts because of their ability to change their oxidation state (oxidation number)
- The Sulphur dioxide is oxidized to Sulphur trioxide by the vanadium (V) oxide
- In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

- The vanadium (IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + \frac{1}{2}O_2 \rightarrow V_2O_5$$

- Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started

[Q]UICK QUIZ-4

[Th]e source of vanadium in +5 oxidation state

[illegible] +5 oxidation state [illegible]m metavanadate, NH_4VO_3

How solution of NH_4VO_3 is prepared

[illegible] Therefore it is usually first dissolved in sodium hydroxide [illegible]

[Ho]w re-oxidation of lower oxidation state of vanadium is prevented

[illegible] oxidation state can be easily re-oxidized by atmospheric oxygen. It can be prevented [illegible] flask and in the presence of [illegible]. Zinc is a reducing agent so it keeps the vanad[ium] [illegible]

How V_2O_5 use as catalyst for oxidation of $SO_2(g) \rightarrow SO_3(g)$

See Page 84

[C]HROMIUM

[Im]portant discussion is,

(i) The interconversion of the various oxidation states of chromium

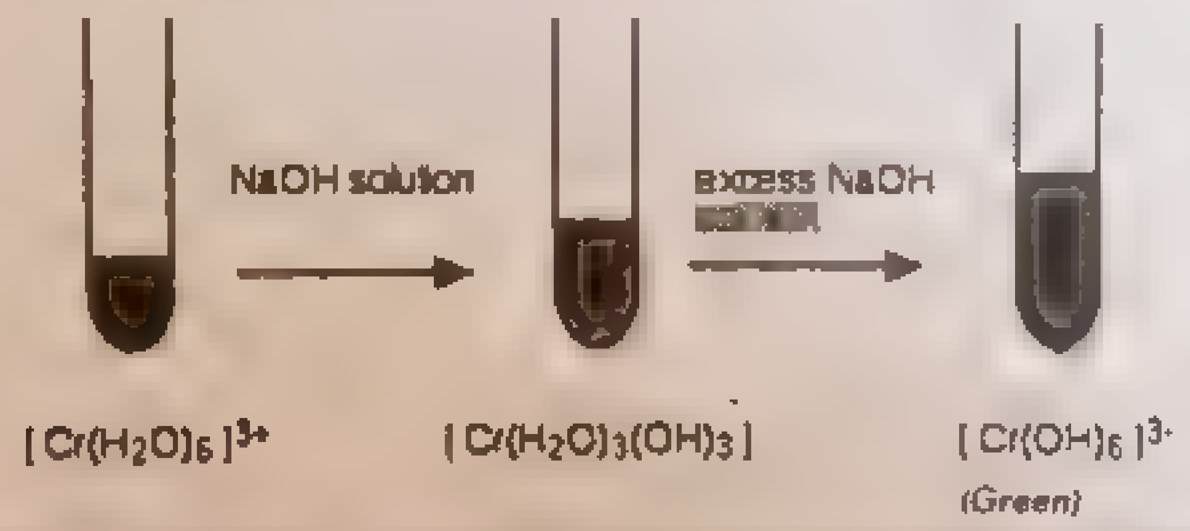
(ii) The chromate (VI)-dichromate (VI) equilibrium

(iii) The use of dichromate (VI) ions as an oxidizing agent (including titrations

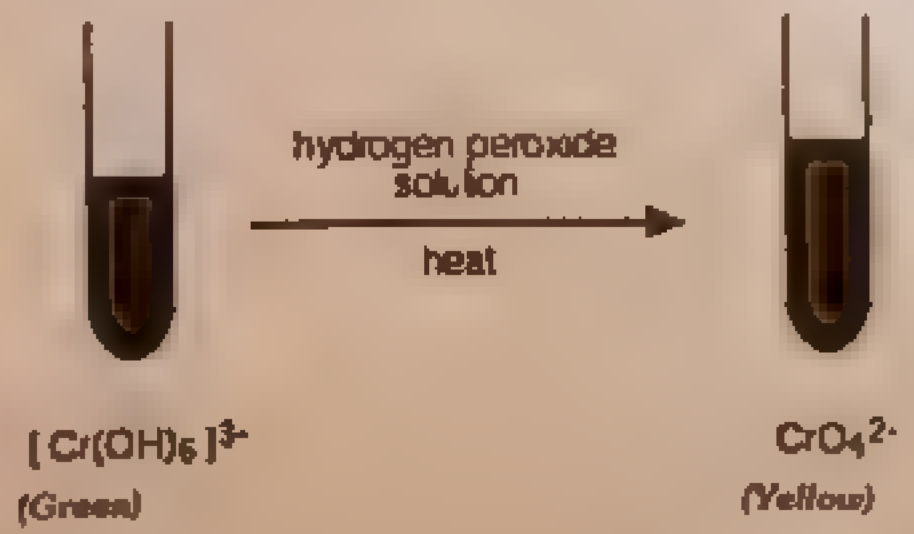
[Ex]ercise Q3(v) (b) How does chromium (III) changes to chromium (VI)?

[T]HE OXIDATION OF CHROMIUM(III) TO CHROMIUM(VI)

- An excess of sodium hydroxide solution is added to a solution of the hexaaq[ua]chromium[(III)] ions [to] produce a solution of green hexahydroxochromate(III) ions.



- This is then oxidized by warming it with hydrogen peroxide solution. Finally a b[ri]g[ht] [yellow] [solution] containing chromate(VI) ions is obtained.



The equation for the oxidation stage is:

$$2[Cr(OH)_6]^{3-} + 3H_2O_2 \rightarrow 2CrO_4^{2-} + 2OH^- + 8H_2O$$

SOME CHROMIUM(VI) CHEMISTRY

THE CHROMATE(VI)-DICHROMATE(VI) EQUILIBRIUM

The colo[illegible]

- oran[illegible]
- yellow [illegible]

These two can be inter[illegible]

- [illegible]
- [illegible]

CrO_4^{2-} Yellow [illegible] Orange

The most Important Precaution

- Let the yellow chromate(VI) ions are just produced [illegible] They cannot be converted into dichromate(VI) ions [illegible]
- In the presence of acid, dichromate(VI) ions react with an[illegible] the original reaction!
- To prevent this, the solution is heated for some time to decom[illegible]gen peroxide into water and oxygen before adding the acid

Explanation of the Chromate-Dichromate equilibrium

- The equilibrium reaction of the interconversion is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- If extra hydrogen ions are added to this, then according to Le Chat[illegible] principle the equ[illegible] the right

Adding hydrogen ions forces the position of equilibrium to the right

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- If hydroxide ions are added, these react with the hydrogen ions. Thus, according to Le-Chatlier's principle the equilibrium shifts to the left to replace them

Adding hydroxide ions removes these hydrogen ions

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

The equilibrium moves to the left to replace hydrogen ions.

REDUCTION OF DICHROMATE(VI) IONS WITH ZINC AND AN ACID

Oxidation state = +6

$Cr_2O_7^{2-}$

- The chromium (III) ions ...
- The equations ...

For the reduction from +6 to +3

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

For the reduction from +3 to +2

$$2Cr^{3+} + Zn \rightarrow 2Cr^{2+} + Zn^{2+}$$

Exercise Q3(c) (c) *Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry.* *(For Potassium manganate (VII) see page 92)*

USING POTASSIUM DICHROMATE (VI) AS AN OXIDIZING AGENT IN ORGANIC CHEMISTRY

- Potassium dichromate(VI) solution acidified with dilute sulphuric acid ... agent in organic chemistry.
- It is a reasonably strong oxidizing agent so that it can take the whole of the ... Potassium manganate(VII) solution also has this tendency.

- It is used to:
  - ✓ oxidize secondary alcohols to ketones,
  - ✓ oxidize primary alcohols to aldehydes,
  - ✓ oxidize primary alcohols to carboxylic acids

Example:

- Ethanol (a primary alcohol), is oxidized to ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) ... on the conditions as given below.

(i) ***Case-I:*** If the alcohol is in excess, the aldehyde is distilled off as soon as it is formed. Thus, ethanal ... main product.

$$Cr_2O_7^{2-} + 8H^+ + 3CH_3CH_2OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$$

e.g.

$$2Cr_2O_7^{2-} + 16H^+ + 3CH_3CH_2OH \rightarrow 4Cr^{3+} + 11H_2O + 3CH_3COOH$$

e.g. The ...

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$
$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

USING POTASSIUM DICHROMATE(VI) AS AN OXIDIZING AGENT IN TITRATIONS

- Pota...
- ...

In practice

There are advantages and disa...

Advantages

- Potassium dichr... known concentr... manganate(VII).
- Potassium dichromate (VI) can be used in the ... ride ions. It is possible if chloride ions are not present in very high conce...
- Potassium manganate(VII) oxidizes chloride ions to chlorine. However, potassium dichromate(VI) is not so strong to do this. It means there are no unwanted side reactions with the potassium dichromate(VI) solution.

Disadvantages

- The main disadvantage lies in the colour change.
- Potassium manganate(VII) titrations are self-indicating. Potassium manganate(VII) solution is purple in colour. When it is run into the given solution, the solution becomes colourless. However, when just one drop is added in excess, the solution becomes pink. Thus, it can be detected easily. This is the end point.
- Potassium dichromate(VI) solution is orange in colour. When it is run into the given solution, the solution turns green. So, when there is one drop of orange solution is in excess in a strongly coloured green solution, the colour change cannot be detected. Hence, with these titrations separate indicators are used known as a *redox indicator*. Therefore, with potassium dichromate(VI) solution separate indicators are used known as a *redox indicator*. These change colour in the presence of an oxidizing agent.
- There are several such indicators; such as diphenylamine sulphonate. This gives a violet-blue colour in the presence of excess potassium dichromate(VI) solution. However, the colour is made difficult by the presence of strong green colour.
- Hence, the end point of a potassium dichromate(VI) titration is not as easy to see as the end point of a potassium manganate(VII) titrations.

The Calculation

The half-equation for the dichromate(VI) ion is:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

and for the iron(II) ions is

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Combining these two ho...

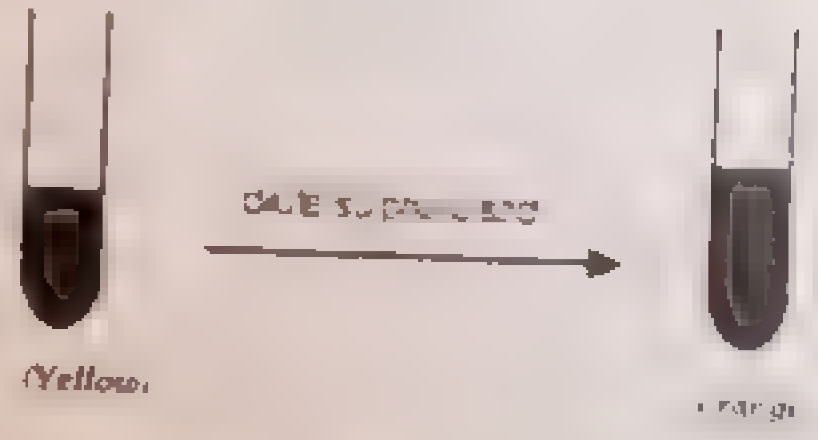
$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

TESTING FOR CHROMATE(VI) IONS IN SOLUTION

- Typically, testing ...
- Most chromates are ...
- The bright yellow co...

Testing by adding an acid

- If some dilute sulphuric ... orange colour of dichr...

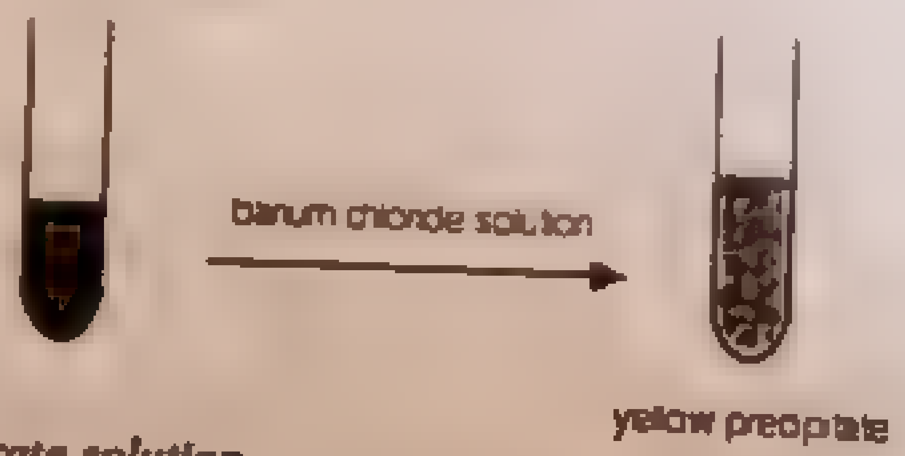


This test cannot be sure for chromate(VI) ions. This colour change ... solution

Testing by adding barium chloride (or nitrate) solution

Chromate(VI) ions will give a yellow precipitate of barium chromate...

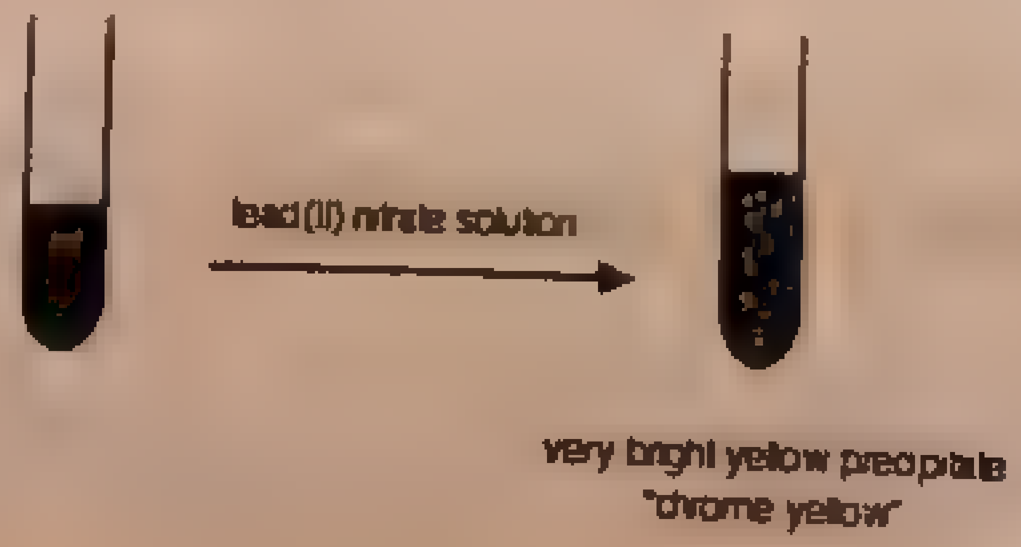
$$Ba^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow BaCrO_{4(s)}$$



Testing by adding lead(II) nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI). $PbCrO_4$ is the original "chrome yellow" paint pigment.

$$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow PbCrO_{4(s)}$$



QUICK QUIZ-5:

(1) How dichromate ion is converted into chromate and vice versa

The equilibrium [illegible]

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Thus

- [illegible] $Cr_2O_7^{2-}$ [illegible]
- [illegible] CrO_4^{2-} ions [illegible] shift the equilibrium to the [illegible]

(2) What happens when chromate ion reacts with barium chloride

The CrO_4^{2-} ions react with Ba^{+2} [illegible] used as a test for Ba^{+2} ions

$$Ba^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow BaCrO_{4(s)}$$

(3) Why potassium dichromate is preferred over potassium manganate in titration

- Potassium dichromate (VI) can be used as a primary standard. It means that its stable [illegible] accurately known concentration can be dire[illegible]
- Potassium dichromate (VI) can be used in the presence of [illegible] chloride ions are not present in very high concentration. Thus, [illegible]

(4) In which titration end point is clear potassium dichromate or potassium magnate

- Potassium dichromate(VI) solution is orange in colour. When it is run into the given solution, the solution turns green. So, when there is one drop of orange solution is in excess [illegible] coloured green solution, the colour change cannot be detected. Hence, with these titrations [illegible] indicators are used, known as a *redox indicator*
- Potassium manganate(VII) solution is purple in colour. When it is run into the given solution, the solution becomes colourless. However, when just one drop is added in excess, the solution becomes pink. Thus, it can be detected easily. This is the end point

(5) What color changes occur when following are added separately in potassium chromate solution

(i) Acid

The equilibrium reaction of the interconversion of CrO_4^{2-} and $Cr_2O_7^{2-}$ ions is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Thus, if dilute sulphuric acid is added to the yellow solution of CrO_4^{2-} ions, it is converted into orange solution of $Cr_2O_7^{2-}$ ions. It is because, the acid provide H^+ ions, which shift the equilibrium to the right

(iii) Lead nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI)

$$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow PbCrO_{4(s)}$$

MANGANESE

This section describes

- The Oxidation States
- Two simple reactions of manganese (II) ions in solution
- The use of potassium manganate(VII) (potassium permanganate) as an oxidizing agent - including its use in titrations

OXIDATION STATES

- Manganese can exist in a number of oxidation states. Its most stable oxidation states are +2, [illegible] 4 [illegible] +[illegible]
- In the +7 oxidation state it exists as the intense purple ion MnO_4^-
- It can be reduced to the pale pink Mn^{2+} by Fe^{2+} in acidic solution

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

> [illegible] Fe^{2+} / Fe^{3+} equation by 5 and then add to the other equation to get the overall reaction

Overall reaction

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

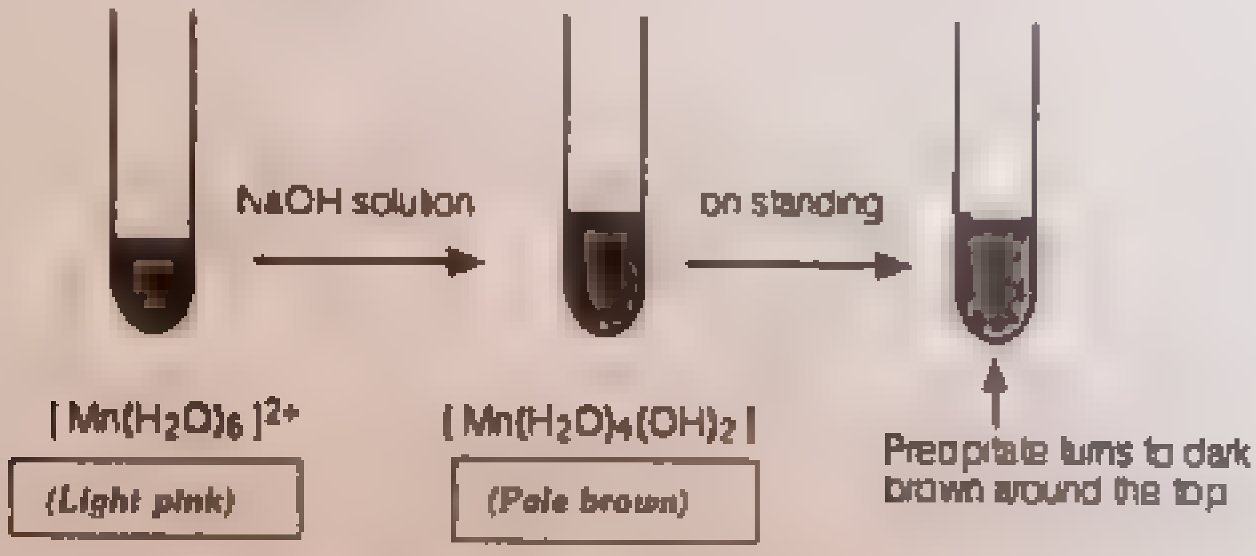
REACTIONS OF MANGANESE (II) IONS IN SOLUTION/ OXIDATION STATES

The reaction of hexaaquamanganese(II) ions with hydroxide ions

- Hydroxide ions (e.g. from sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion.
- Once a hydrogen ion has been removed from two of the water molecules, a complex is formed with no charge (a neutral complex). This is insoluble in water and a precipitate is formed

$$[Mn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

- *In the test-tube, the colour changes are.*

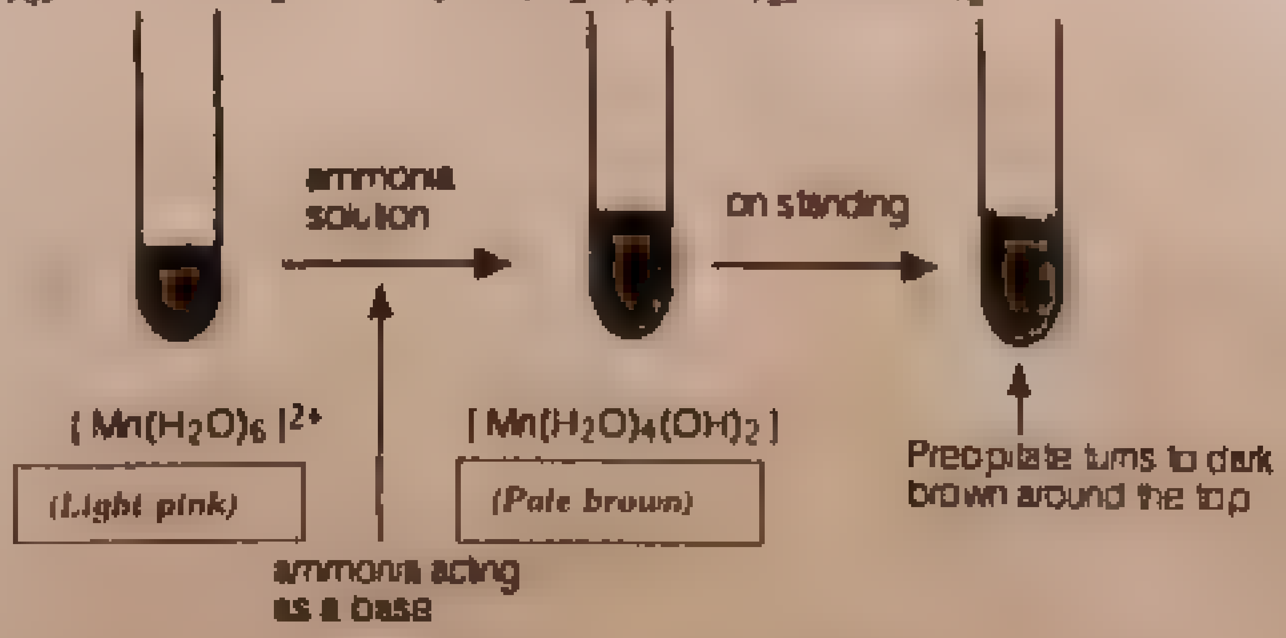


- The original solution is as very light pink as colourless.
- When this reaction occurs, the pale brown precipitate of $Mn(H_2O)_4(OH)_2$ are formed. These [illegible] darker brown manganese(III) oxide on contact with oxygen from the air

The reaction of hexaaquamanganese(II) ions with ammonia solution

- Ammonia can act as both a base and a ligand.
- In this case, it simply acts as a base at usual concentrations. Thus, it removes hydrogen ions from the aqua complex.

$$[Mn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Mn(H_2O)_4(OH)_2] + 2NH_4^+$$



- The original solution is as palest pink as colourless
- The pale brown precipitate is oxidized to darker brown manganese ... the air
- There is no observable difference in appearance between this reaction and the last one

SOME POTASSIUM MANGANATE(VII) CHEMISTRY

Exercise Q3(v) (c) Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry. *(For Potassium dichromate (VI) see page 87)*

Potassium manganate(VII) (potassium permanganate) is a powerful oxidizing agent.

(i) Using potassium manganate(VII) as an oxidizing agent in organic chemistry

- Potassium manganate (VII) is usually used as oxidizing agent in neutral or alkaline ... chemistry
- Acidified potassium manganate(VII) is somewhat destructive strong oxidizing agent, ... bonds
- The potassium manganate(VII) solution is usually made mildly alkaline with sodium carbonate ... typical colour changes are:

(ii) In testing for a C=C double bond: Baeyer's Test

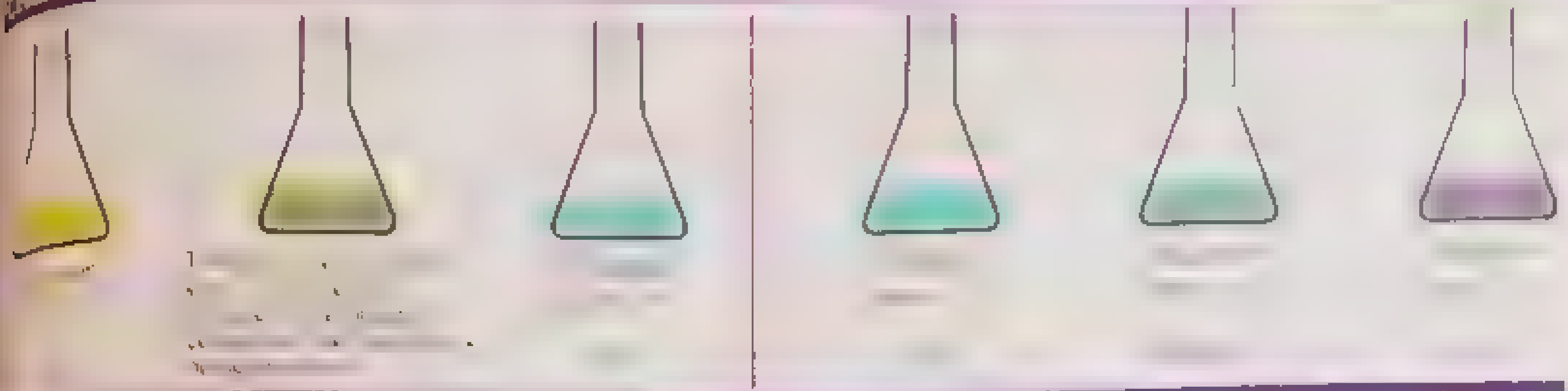
Potassium manganate(VII) oxidizes carbon-carbon double bonds and goes through the ... above

e.g. Ethene is oxidized to ethane-1,2-diol (ethylene glycol)

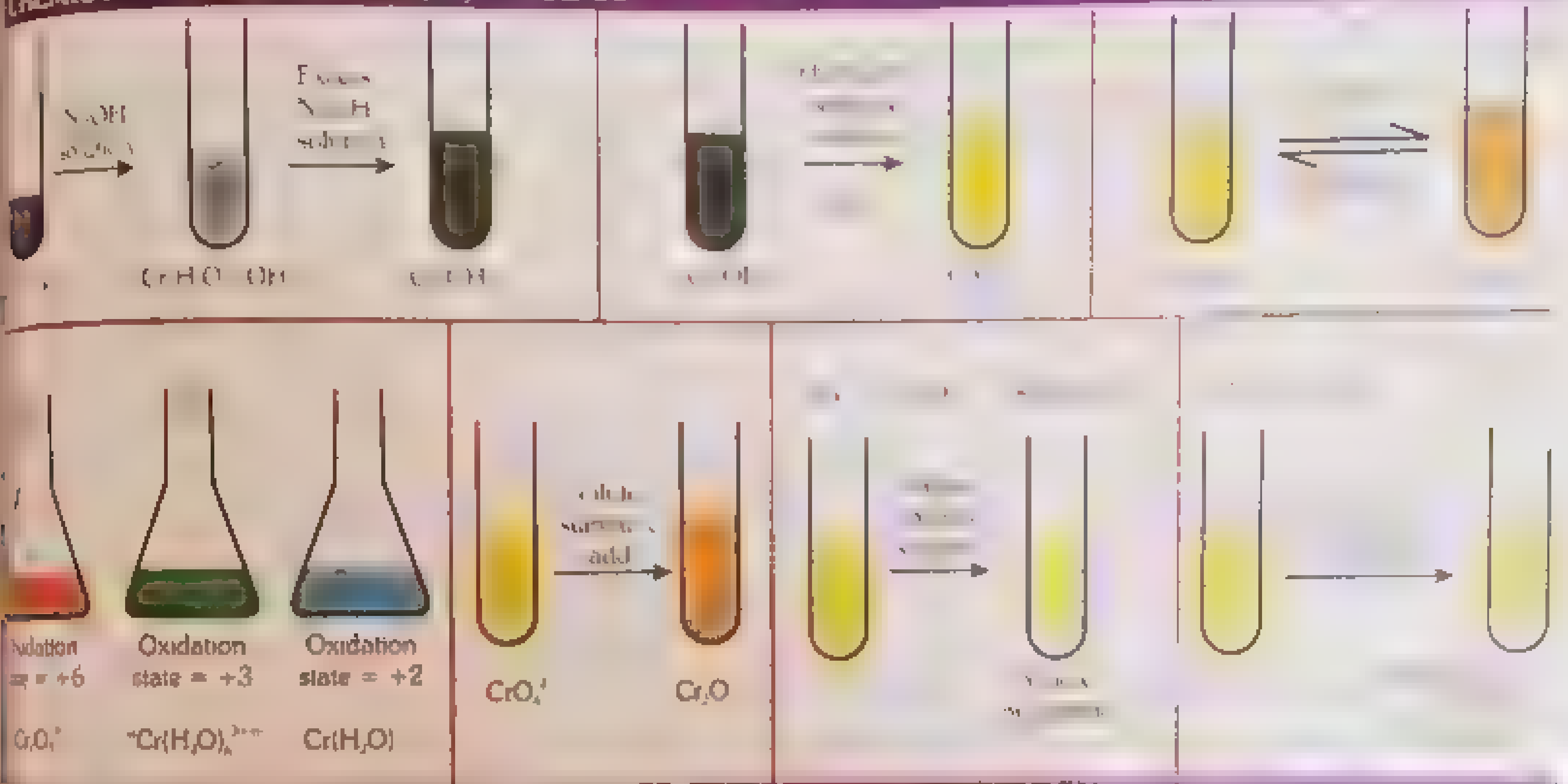
$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2O + [O] \longrightarrow \underset{\text{Ethane-1,2-diol}}{CH_2(OH)-CH_2(OH)}$$

- This abbreviated form of the equation is most commonly used in organic chemistry. The complete ... equation for this reaction is generally not written.
- *The oxygen in square brackets is taken to mean "oxygen from an oxidizing agent"*
- *It is not a good test for a carbon-carbon double bond. It is because even any mild reducing species ... same effect on the potassium manganate(VII) solution.*
- However, this reaction can be simply used to prepare the diol.

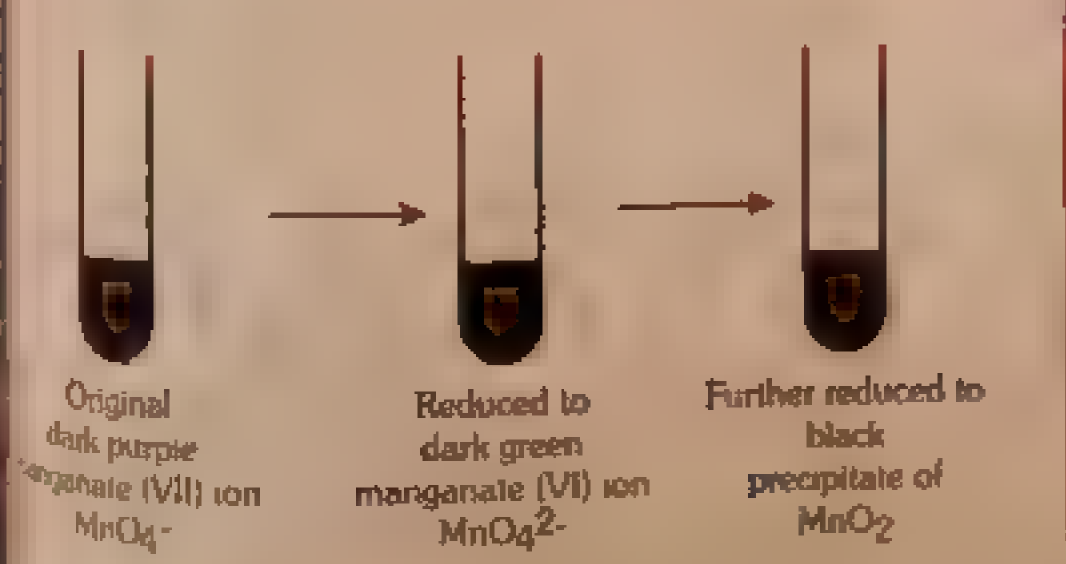
CHEMISTRY OF VANADIUM (V): PAGE 81



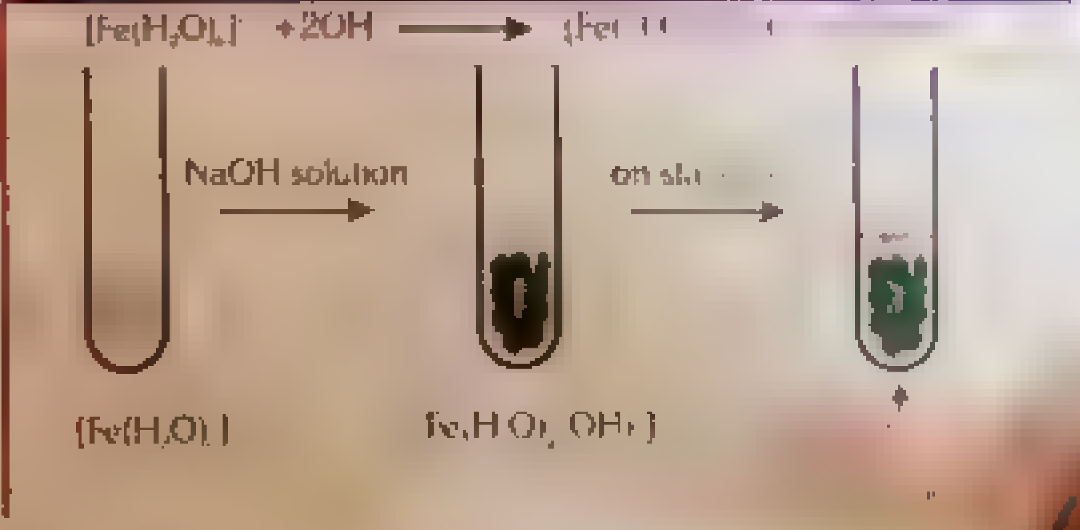
CHEMISTRY OF CHROMIUM (Cr): PAGE 85



CHEMISTRY OF MANGANESE (Mn): PAGE 90



CHEMISTRY OF IRON (Fe): PAGE 95



[illegible]

CHEMISTRY OF COPPER (Cu, PAGE 9)

FLAME COLOURS (PAGE 27)

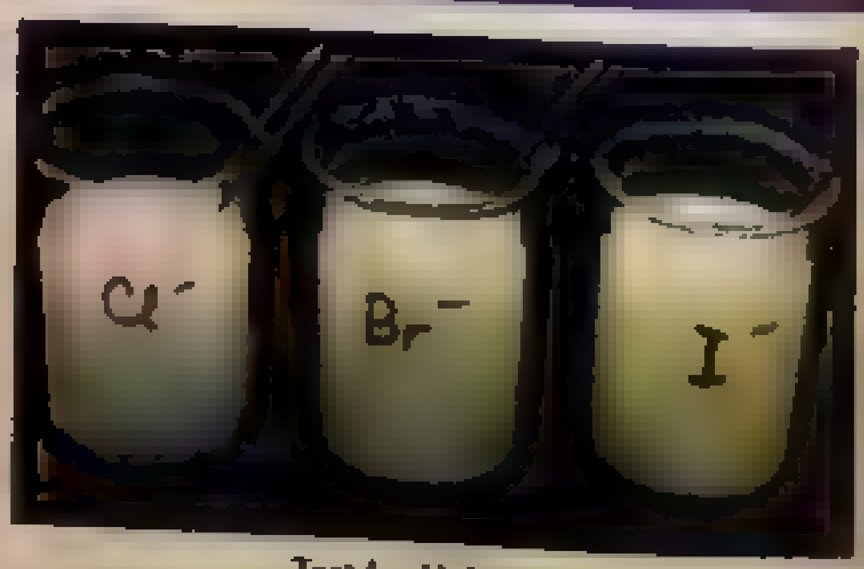
Li	Na	K	Rb	Cs	Ca	Sr	Ba	Cu	Pb
Red	[illegible]	[illegible]	Reddish violet	Blue	Brick red	Red	Pale green	Blue green	(greyish white)

LASSAIGNE'S TEST (PAGE 120)

Test for N
(Prussian blue colour

Test for N + S
Blood Red colour

Test for S
Black ppt.)

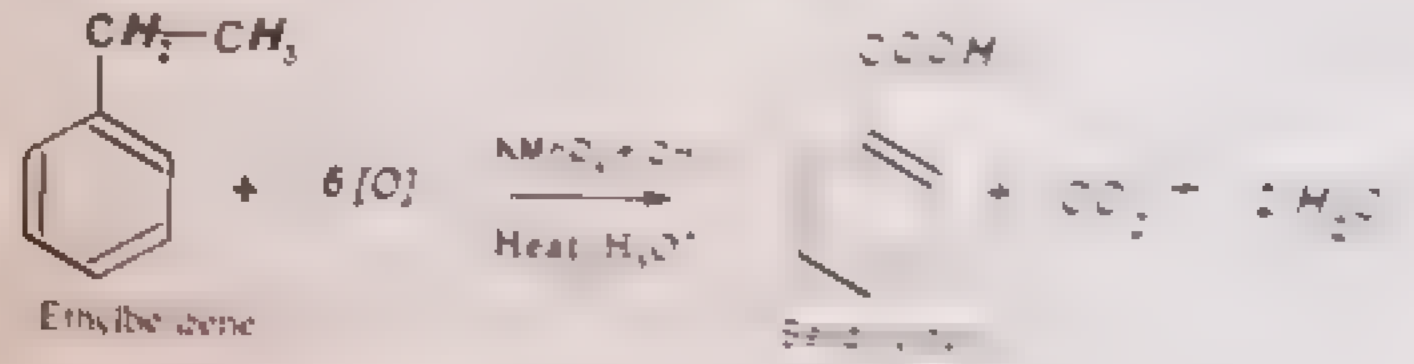


Test for Halogens
(White = Cl⁻, Pale yellow = Br⁻, Yellow = I⁻)

(ii) In the oxidation of aromatic side chains

- Alkaline potassium ma... to -COOH group. Prolonged ...

Examples



- In the case of the ethyl side chain ...
- With longer side chains you will get a ...
- However, in each case, the main product ...

USING POTASSIUM MANGANATE(VII) AS AN OXIDIZING AGENT IN TITRATIONS

Background

- Potassium manganate(VII) solution is used to ...
- It is always used in acidic solution

Examples: It oxidizes

- iron(II) ions to iron(III) ions

  $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- hydrogen peroxide solution to oxygen

  $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
- Ethanedioic acid to carbon dioxide (This reaction has to be done ...

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \rightarrow 2CO_2 + 2H^+ + 2e^-$$

- Sulphite ions (sulphate(IV) ions) to sulphate ions (sulphate(VI) ions)

  $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$
- In each case, the half equation for the manganate(VII) ions in acidic solution is

  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
- These equations can be combined to give you an overall ionic equation for each possibility.
- From the overall reaction the reacting proportions (mole ratio) is also obtained.

  e.g., Add the Fe^{2+} ions oxidation reaction to the MnO_4^- ions multiplying by suitable numbers.

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$
$$\underline{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$$
$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Thus, the reacting proportion is:

1 mole of permanganate(VII) ions : 5 moles of iron(II) ions. This mole ratio can be used for titration calculations.

Doing the titration

- The potass[illegible] solution always taken in the burette
- The [illegible]
- As [illegible]
- Whenever [illegible] excess of manganate [illegible] appears. [illegible]

Problems with the use of potassium manganate (VII) solution

- Potassium manganate(VII) cannot be used [illegible] because it [illegible] side reactions [illegible] hydrochloric acid [illegible]
- Potassium manganate(VII) is not a primary standard. It means that a stable solution of accurately known concentration cannot be directly prepared by weighing it.
- Actually, it is [illegible] Moreover, it [illegible] the water [illegible] oxidized [illegible]
- Bottles of potassium manganate [illegible] manganese (IV) oxide. It is produced when the manganate [illegible]
- So, first a solution of approximate concentration is prepared a [illegible]
- This standardization is often done by titration with ethanedioic acid (oxalic acid) [illegible] is a primary standard.

QUICK QUIZ 6

(1) Give half equation for manganate (VII) ion in acid solution.

The half-equation for the manganate(VII) ions in acidic solution is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

(2) Write equation for oxidation of oxalic acid

Ethanedioic acid (oxalic acid) is oxidized by $KMnO_4$ to carbon dioxide. This reaction has to be done hot.

The half-equation for oxalic acid is

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} \rightarrow 2CO_2 + 2H^+ + 2e^- \quad \text{\_\_\_\_(1)}$$

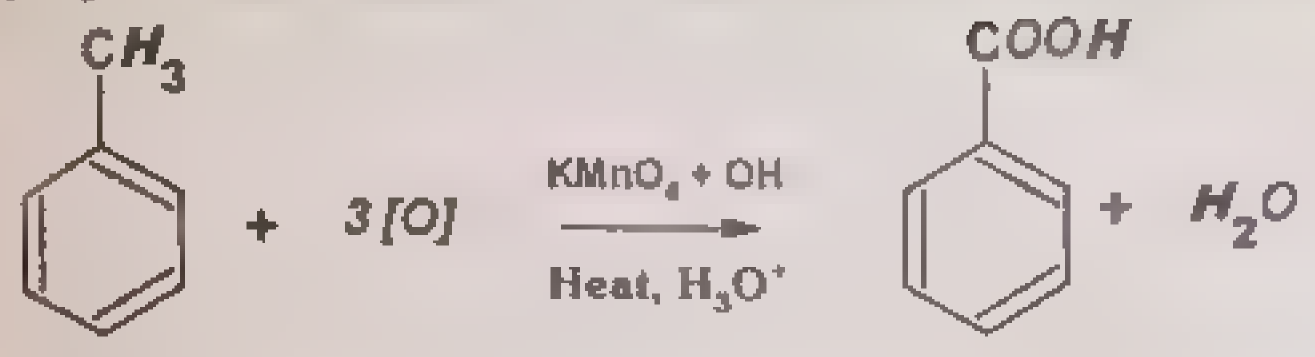
The half-equation for MnO_4^- is

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{\_\_\_\_(2)}$$

Multiplying equation (1) by 5, equation (2) by 2 and then adding them gives the overall reaction

$$5\begin{array}{c} COOH \\ | \\ COOH \end{array} + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$$

(3) *How can you convert toluene into benzoic acid*



Toluene Benzoic acid

(4) *Write equation of reaction of hexaaquamanganate(II) with ⁻OH ion. What color change is observed*

The equation is

$$[Mn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Mn(H_2O)_4(OH)_2] + 2H_2O$$

- The original solution is as very light pink as colourless.
- When this reaction occurs, the pale brown precipitate of $Mn(H_2O)_4(OH)_2]$ are formed. These are oxidized to darker brown manganese(III) oxide on contact with oxygen from the air.

IRON

The important points are:

(i) Oxidation state

(ii) Iron as catalyst in Haber's Process and in reaction between per sulphate and iodide ions

(iii) Reaction of Hex aqua Iron (II) and (III) with water, ammonia, Carbonate and Thiocyanate ions

OXIDATION STATE

- Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+})
- In aqueous solution, the Fe is readily oxidized from Fe^{2+} to Fe^{3+}

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$$

- The Fe^{2+} ion is thus a reducing agent.
- Thus, concentrations of Fe^{2+} in solution can be determined by titration with oxidizing agents.

IRON AS CATALYST IN THE HABER PROCESS

- The Haber process combines nitrogen and hydrogen into ammonia
- The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane
- Iron is used as a catalyst.

$$N_{2(g)} + 3H_{2(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3(g)}$$

IRON IONS AS A CATALYST IN THE REACTION BETWEEN PERSULPHATE IONS AND IODIDE IONS

- The reaction between persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, and iodide ions in solution can be catalyzed using either iron(II) or iron(III) ions.
- The overall equation for the reaction is:

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

- Let the catalyst is iron(II) ions.
- The reaction occurs in two stages.

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$$

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

- If iron(III) ions are used then the second of these reactions occurs first.
- This is another example of the transition metal compounds to act as catalysts because of their ability to change oxidation state.

REACTIONS OF IRON IONS IN SOLUTION

The simplest ions [illegible]

- the hexaaqua[illegible] $[Fe(H_2O)_6]^{2+}$
- the hexaaquairo[illegible] on $[Fe(H_2O)_6]^{3+}$

(i) Reactions of the iron ions with hydroxide ions

- Hydroxide ions (e.g. from sodium hydroxide [illegible] ligands attached to the iron ion [illegible]
- Once enough hydrogen ion has bee[illegible] the water molecules, a complex is formed with no charge (a neutral [illegible]

In the iron(II) case

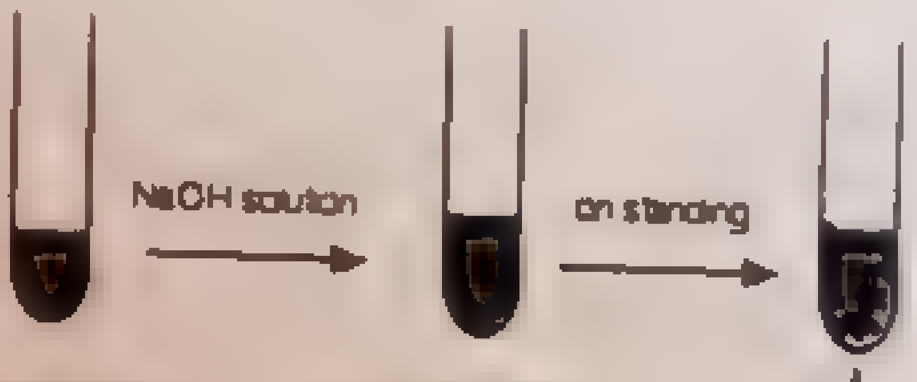
$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(H_2O)_4(OH)_2] + 2H_2O$$

In the iron(III) case

$$[Fe(H_2O)_6]^{3+} + 3OH^- \rightarrow [Fe(H_2O)_3(OH)_3] + 3H_2O$$

- In the test-tube, the colour changes are

In the iron(II) case



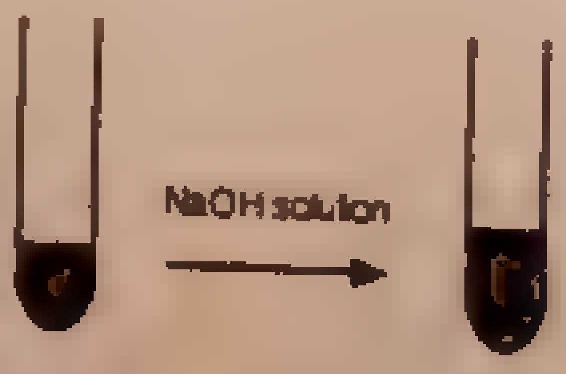
$[Fe(H_2O)_6]^{2+}$ *(Green solution)*

$[Fe(H_2O)_4(OH)_2]$ *(Green precipitates)*

Precipitate darkens and turns orange around the top

- Iron is very easily oxidized under alkaline conditions
- Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube.
- The darkening of the precipitate comes from the same effect.

In the iron(III) case:



$[Fe(H_2O)_6]^{3+}$ *(Yellow solution)*

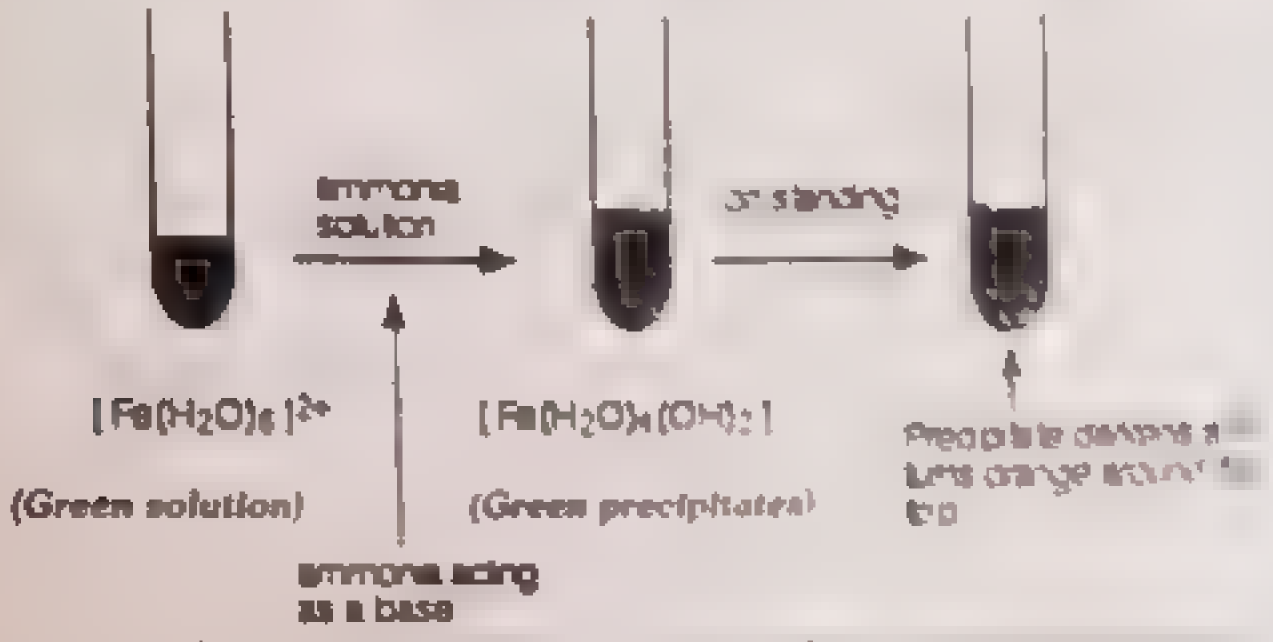
$[Fe(H_2O)_3(OH)_3]$ *(Orange precipitates)*

Reactions of the iron ions with ammonia solution

- Ammonia can act as both a base and a ...
- In these cases, it simply acts as a base. ...

In the iron(II) case:

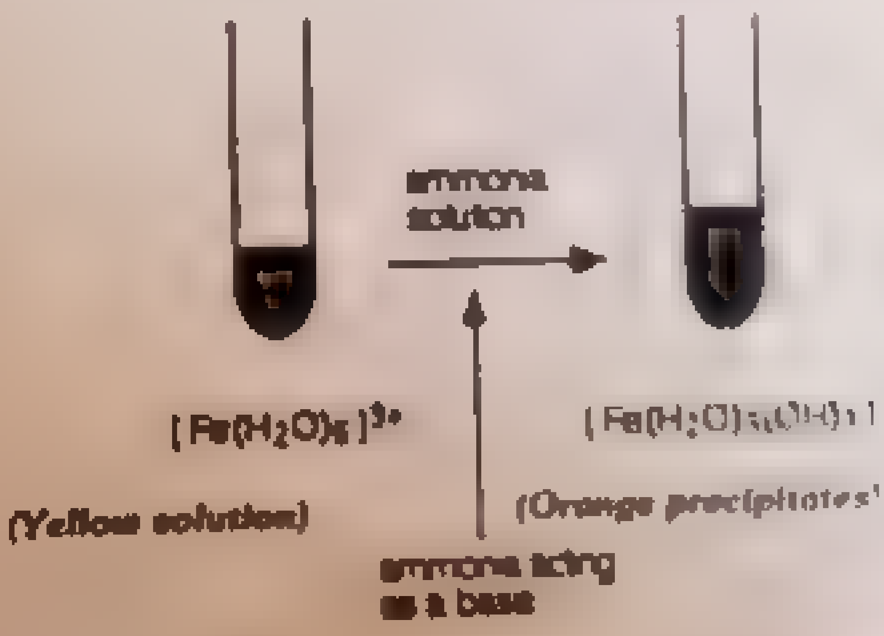
$$[Fe(H_2O)_6]^{2+} \quad + \quad 2NH_3 \quad \rightarrow \quad [Fe(H_2O)_4(OH)_2] \quad + \quad 2NH_4^+$$



- The appearance is just the same as in when you add sodium hydroxide ...
- The precipitate again changes colour as the iron(II) hydroxide ... hydroxide

In the iron(III) case:

$$[Fe(H_2O)_6]^{3+} \quad + \quad 3NH_3 \quad \rightarrow \quad \underset{(orange)}{[Fe(H_2O)_3(OH)_3]} + 3NH_4^+$$



The reaction looks just the same as when you add sodium hydroxide solution.

(iii) Reactions of the iron ions with carbonate ions

There is an important difference here between the behaviour of iron(II) and iron(III) ...

(a) Iron(II) ions and Carbonate ions

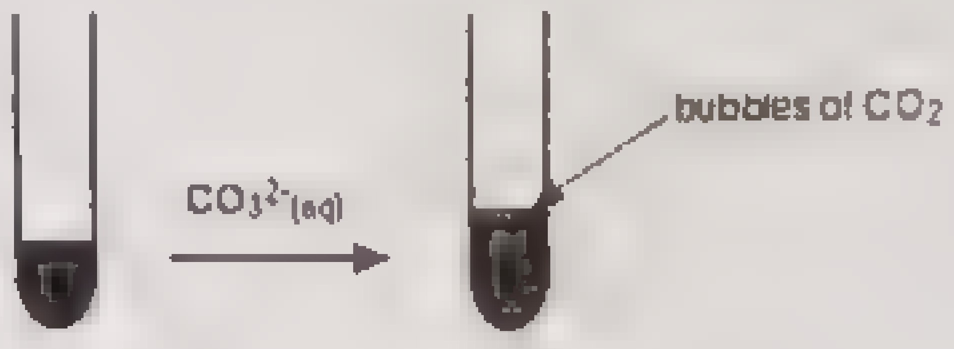
The precipitates of iron(II) carbonate are produced

$$Fe^{2+}_{(aq)} + CO_3^{2-} \rightarrow FeCO_{3(s)}$$

(b) Iron(III) Ions and Carbonate Ions

- The hexaaquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.
- If sodium carbonate solution is added to a solution of hexaaquairon(III) ions, the same precipitate is obtained as with sodium hydroxide solution or ammonia solution
- This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex
- Depending on the proportions of carbonate ions to hexaaqua ions, there are two possibilities for the products
  - ✓ either hydrogencarbonate ions are formed
  - ✓ or carbon dioxide gas is formed from the reaction between the hydrogen ions and carbonate ions
- The more usually quoted equation shows the formation of carbon dioxide

$$2[Fe(H_2O)_6]^{3+} + 3CO_3^{2-} \rightarrow \underset{(orange)}{2[Fe(H_2O)_3(OH)_3]} + 3CO_2 + 3H_2O$$



$[Fe(H_2O)_6]^{3+}$ *(Yellow solution)* $[Fe(H_2O)_3(OH)_3]$ *(Orange precipitates)*

(iv) Testing for Iron(III) Ions with thiocyanate Ions

- This provides an extremely sensitive test for iron(III) ions in solution
- If thiocyanate ions, SCN^- ions (e.g. from sodium or potassium or ammonium thiocyanate solution) are added to a solution containing iron(III) ions, an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$ is formed

solution containing $[Fe(H_2O)_6]^{3+}$ *(Yellow solution)* $[Fe(SCN)(H_2O)_5]^{2+}$ *(Blood red solution)*

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

These combine to give the ionic equation for the reaction

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

QUICK QUIZ-7

1) Give role of ammonia in reaction of it [illegible]

[illegible]

In the iron(II) case

$$[Fe(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Fe(H_2O)_4(OH)_2] + 2NH_4^+$$

In the iron(III) case

$$[Fe(H_2O)_6]^{3+} + 3NH_3 \rightarrow [Fe(H_2O)_3(OH)_3] + 3NH_4^+$$

***2) In which form iron ion are present** in aqueous solution*

Iron exists in [illegible]

- the hexaaqua[illegible] $[Fe(H_2O)_6]^{2+}$
- the hexaaqua[illegible] $[Fe(H_2O)_6]^{3+}$

3) Write reaction equation between persulphate ion and iodide ion

- The overall equation for the reaction is

$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$

- This reaction can be catalyzed by iron ions. The rea[illegible]

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

- If iron(III) ions are used then the second of these reactions [illegible]

4) How thiocyanate ion is used for testing of Fe?

If thiocyanate ions, SCN^- ions are added to a solution containing [illegible] containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$ is formed. The reaction is

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightarrow [Fe(SCN)(H_2O)_5]^{2+} + H_2O$$

SCN^- ions are added as sodium or potassium or ammonium thiocyanate [illegible]

COPPER

The important discussion includes

(i) The Oxidation States

(ii) The reaction of hexaaquacopper (II) ions with hydroxide ions, Ammonia and Carbonate [illegible]

THE OXIDATION STATES

- Copper exists in two common oxidation states, +1 (Cu^{1+}) and +2 (Cu^{2+}).
- In aqueous solution, the Cu is readily oxidized from Cu^{1+} to Cu^{2+}:

$$Cu^{1+}(aq) \rightarrow Cu^{2+}(aq) + e^-$$

- The Cu^{1+} ion is thus a reducing agent.
- Thus, concentrations of Cu^{1+} in solution can be determined by titration with oxidizing agents.

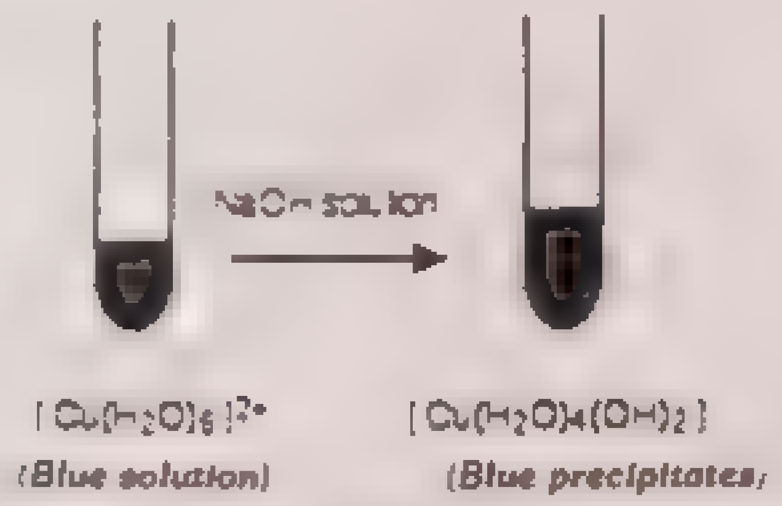
THE REACTION OF HEXAAQUACOPPER(II) IONS WITH HYDROXIDE IONS

- [illegible] e.g. [illegible] hydroxide solution remove hydrogen ions from the water ligands [illegible]
- [illegible] removed from two of the water molecules, a complex [illegible] with no [illegible] water and a precipitate is formed
- T[illegible] water and a precipitate is formed

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow [Cu(H_2O)_4(OH)_2] + 2H_2O$$

(blue

- In the test tube the colour changes [illegible]



REACTIONS OF HEXAAQUACOPPER(II) IONS WITH AMMONIA SOLUTION

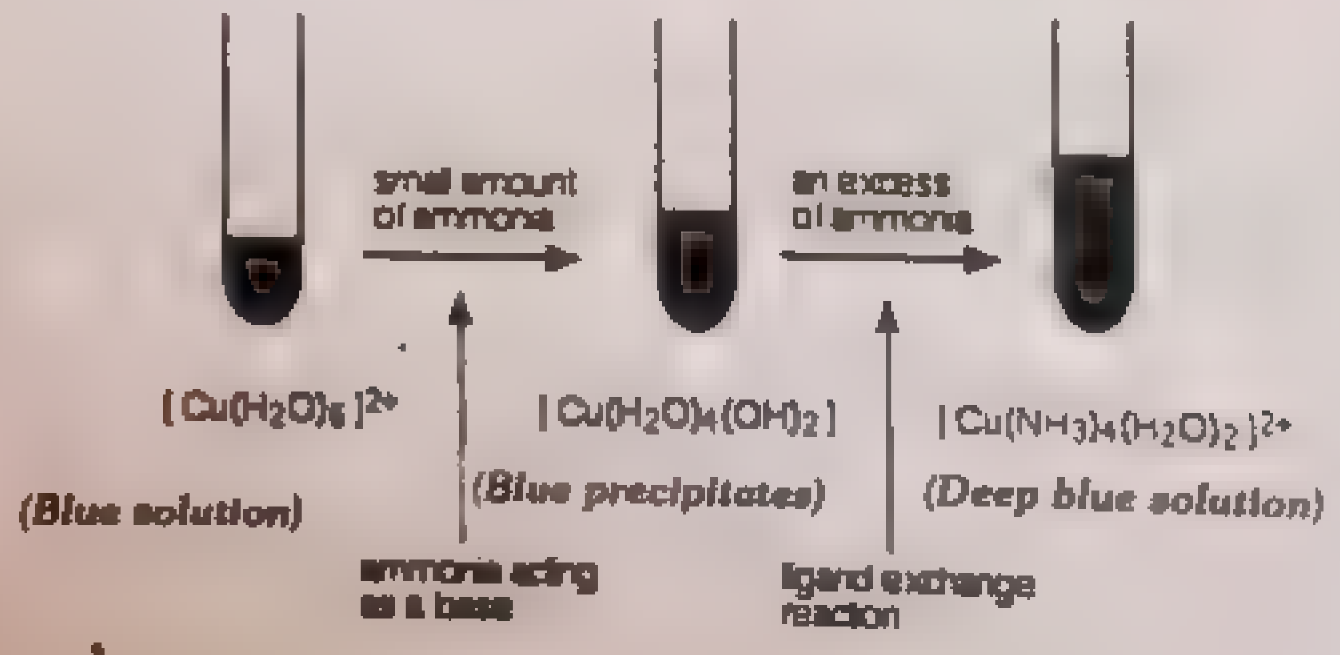
- Here, the ammonia acts both as a base and as a ligand
- With a small amount of ammonia hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex. This is insoluble and precipitates are formed

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

- The precipitate dissolves by adding an excess of ammonia
- The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions
- Notice that only 4 of the 6 water molecules are replaced

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

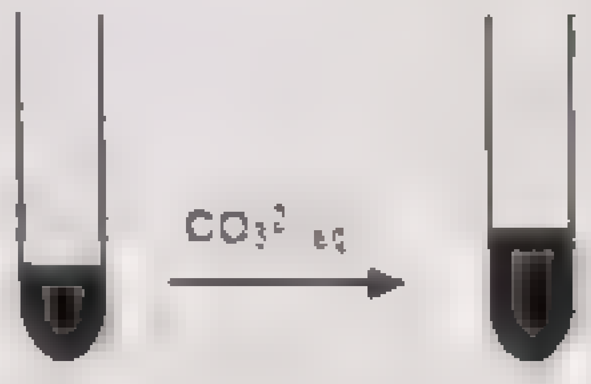
- *The colour changes are:*



REACTION OF HEXAAQUACOPPER(II) IONS WITH CARBONATE IONS

The precipitates of copper(II) carbonate are obtained

$$Cu^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow \underset{(blue)}{CuCO_{3(s)}}$$



$[Cu(H_2O)_6]^{2+}$ *(Blue solution)* "$CuCO_3$" *(Blue precipitates)*

QUICK QUIZ-8:

Ammonia acts as base as well as ligand. Prove above statement by reaction with copper ion.

- Copper ions exist as hexaaqua complex in water
- With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion to give the same neutral complex. This is insoluble and precipitates are formed. Here ammonia is acting as a base

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$$

- The precipitate dissolves by adding an excess of ammonia. The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Here, ammonia is acting as a ligand

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

- Only 4 of the 6 water molecules are replaced

When copper ion reacts with carbonate. What you expect. Which types of precipitate are formed?

The precipitates of copper(II) carbonate are obtained when copper (II) ions react with a carbonate

$$Cu^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow \underset{(blue)}{CuCO_{3(s)}}$$

This reaction is used as a test for copper (II) ions.

Cu^{+1} ion is reducing/oxidizing agent and why?

- Copper exists in two common oxidation states, +1 (Cu^{1+}) and +2 (Cu^{2+})
- In aqueous solution, the Cu is readily oxidized from Cu^{1+} to Cu^{2+}

$$Cu^{1+}(aq) \rightarrow Cu^{2+}(aq) + e^-$$

- The Cu^{1+} ion is thus a reducing agent.

SOCIETY, TECHNOLOGY AND SCIENCE

[illegible]

- [illegible]
- [illegible]

Name of Compound	Uses
Lead Monoxide	[illegible]
Lead Suboxide	[illegible]
Lead Dioxide	[illegible]
Triplumbic tetra oxide (Red Lead)	[illegible]
Basic Lead Carbonate	(i) It is used as [illegible] (ii) It is used [illegible]

EXERCISE

Select the right answer from the choices given with each question.

...age metals are actually

...is a transition elements but it does not show variable valency because

It has completely ...

Which of the following is non typical transition element

Which elements form alloy

(a) Alka...

Which are repelled by magnetic filed

(a) Paramagnetic

Magnetic moment ... of an atom ...

(a) Electron

The unit of Magnetic moment is

(a) Coulombs (Q)

Bronze alloy contains

(a) Cu and Sn

Give the systematic name for $Fe(CO)_5$

(a) Pentacarbonyl iron (III)

(c) Pentacarbonyl iron ...

Give the chemical formula of a complex compound sodium monochloropenta... (III)

(a) $[Na_3FeCl(CN)_5]$ (b) Fe [NaCl ...

The complexes having coordination number (C.N) ... have geometry

(a) Tetrahedral

If we add HNO_3 to the original vanadium (II) solution, it produces

(a) blue ions (b) ...

Which metal oxide is used in contact process as a catalyst

(a) Cr (b) Mn

In oxidation of chromium (III) to chromium (VI) the green color will change into

(a) colorless (b) bright yellow

Acidified potassium permanganate act as a strong

(a) oxidizing agent (b) reducing agent

Following element shows maximum number of oxidation states?

(a) Mn (b) Fe (c) ...

The color of Mn^{2+} in hydrated form is:

(a) Blue (b) Yellow (c) Light Pink

Which of the following metals show more than one oxidation state?

(a) Al (b) Mg (c) Fe

Iron is used as a catalyst in:

(a) Birkland Process (b) Contact Process (c) Haber Process

During the reaction of Ammonia with iron, it acts as both a base and a.

(a) Ligand (b) Acid (c) Iron

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) Transition metals

Coinage metals are actually Cu, Ag and Au. These are transition elements.

(ii) Ans: (c) It has completely filled d-subshell

The electronic configuration of $_{30}Zn$ is ... Thus, it has completely filled d-subshell. So it ... +2 oxidation state due to lose of $2e^-$ from 4s ...

(iii) Ans: (c) Zn

... because it has completely filled d-subshell. The electronic configuration of $_{30}Zn$ is $[Ar]\ 4s^2\ 3d^{10}$.

(iv) Ans: (d) Transition elements

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice

(i) Ans: (c) Diamagnetic

(ii) Ans: (a) Electron

(iii) Ans: (c) Bohr magneton (BM)

(iv) Ans: (a) Cu and Zn

(v) Ans: (c) Pentacarbonyl iron (0)

(vi) Ans: (c) $Na_4[Fe(CN)_6]$

(vii) Ans: (d) both a and c

(viii) Ans: (c) blue

(xiii) Ans: (c) V

(xiv) Ans: (b) bright yellow

... exist as CrO_4^{2-}

(xv) Ans: (d) oxidizing agent

(xvi) Ans: (c) Mn

... subshell ... subshell ... states

(xvii) Ans: (c) Light Pink

(xviii) Ans: (c) Fe

... unpaired ... variable

(xix) Ans: (c) Haber Process

$N_2 + 3H_2 \rightarrow 2NH_3$

(xx) Ans: None of these

... and ... complex ...

Q2: Give brief answers for the following questions.

(i) Why are d-block elements called transition elements?

They are ... p-block ... s ...

(ii) Why do the d-block elements show different oxidation states?

They show variable oxidation states ... purpose of bond formation ... for the ... and ns orbitals are very close in energy ... (n-1) d ... are as easily lost as ns electrons. Thus d-block elements show different oxidation states.

(iii) Why does Mn show the maximum number of oxidation states in 3d-series?

It is because, Mn has two electrons in 4s ... Generally, greater the number of unpaired ... Mn can use 2 to 7

electrons in bond formation. H...
oxidation states of Mn are. +2, +3, +4

What is the difference between double salts and coordination or complex compounds?

A double salt contains two salts cry...
e.g. potash alum, K_2SO_4. $Al_2(SO_4)_3$...

A complex compounds contain...
ordinate covalent bonds
e.g. $K_4[Fe(CN)_6]$

A double salt does not contain co...

Explain the following terms

(a) Ligand

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand

Examples:

1. In $K_4[Fe(CN)_6]$ ...
2. $[Cu(NH_3)_4]SO_4$ and ...

(b) Coordination Sphere

The central neutral atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral

Examples:

- In $K_4[Fe(CN)_6]$, the ion $[Fe(CN)_6]^{-4}$ is the ...
- In $[Cu(NH_3)_4]SO_4$, the ion $[Cu(NH_3)_4]^{+2}$ is the ...

(c) Central Metal.

The metal atom or ion is usually a transition element. It is surrounded by a number of ligands

Examples:

- In $K_4[Fe(CN)_6]$,
  Fe^{+2} is the central metal ion. Six ligands (CN^- ions) are surrounded ...
- In $[Cu(NH_3)_4]SO_4$,
  Cu^{+2} is the central metal ion. Four ligands (NH_3 ions) are surrounded ...

How chromate ions are converted into dichromate ions?

The equilibrium reaction of the inter-conversion is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

If an acid is added then extra H^+ ions are added to this equilibrium. Hence according to Le Chatelier's principle, the equilibrium shifts to the right. Thus, chromate ions are converted into dichromate ions.

Adding hydrogen ions forces the position of equilibrium to the right

Hydrog

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

[illegible] between paramagnetism and diamagnetism?

- [illegible] magnetic field are called paramagnetic and the phenomenon is called [illegible] the unpaired electrons present in the substances. **e.g.** Mn^{+2} ions
- [illegible] repelled by magnetic field are called diamagnetic and the phenomenon is [illegible] in substances in which even number of electrons are present and thus have [illegible] e.g. [illegible]

[illegible] What are advantages of *Potassium dichromate in titrations?*

- Potassium dichromate (VI) can be used as a primary standard. It means that its stable solution of accurately [illegible] concentration can be directly prepared by weighing it.
- Potassium dichromate (VI) can be used in the presence of chloride ions. It is possible if chloride ions are not present in very high concentration. Thus, no unwanted side reactions occurs.

(x) How does dichromate ion converted into chromate ions.

- The equilibrium reaction of the interconversion is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- If hydroxide ions are added to this equilibrium, these react with the hydrogen ions. Thus according to Le-Chatelier's principle, the equilibrium shifts to the left to replace them. Hence, dichromate ions are converted into chromate ions.

Hydroxide io

Adding hydroxide ions removes these hydrogen ions

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

The equilibrium moves to the left to replace hydrogen ions

Q3: Give detailed answers for the following questions.

(i) (a) What is the valence shell configuration of transition elements? How does it affect the following properties?

(i) Binding energy (ii) Paramagnetism (iii) oxidation states

See Page 69, 70

(b) What are typical and non-typical transition elements?

See Page 67

(c) Explain catalytic Activity of transition elements

See Page 71

(d) Write composition, properties and uses of Brass, Bronze and Nichrome alloys

See Page 72

(ii) (a) Explain different types of ligand with examples

(b) Describe the rules for naming the coordination complexes with examples

See Page 76

(iii) (a) Explain shapes and origin of colors of coordination compounds

See Page 74

(b) Relate the coordination number of ions to the crystal structure of the compound [illegible] are a part

a) Write systematic names to following complexes

(i) $[Co(NH_3)_6]Cl$

(ii) $[Fe(H_2O)_6]$ [illegible]

(iii) $Na_3[CoF_6]$

(iv) $[Cr(OH)_3(H_2O)_3]$

(v) $K_2[PtCl_6]$

(vi) $[Pt(OH)_2(NH_3)_4]SO_4$

(vii) $K_3[Cu(CN)_4]$

(viii) $Na_2[NiCl_4]$

(ix) $Pt(NH_3)_2Cl_4$

(x) $[Ag(NH_3)_2]Cl$

b) Write chemical formulae [illegible]

(i) Potassium hexacyano [illegible]

(ii) Sodium tetrachloronickel [illegible]

(iii) Tetrammine copper [illegible] Sulphate

(iv) Potassium hexachloroplatinate [illegible]

(v) Dichlorotetrammine cobalt [illegible]

a) Discuss vanadium (V) oxide as [illegible]

See Page [illegible]

b) How does chromium (III) changes to chromium [illegible]

See Page 84

c) Discuss potassium dichromate (VI) and Potass[illegible] chemistry

See Page [illegible]

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Marks: 17

... A, B, C, D. Each part carries one mark

i. ... general electronic configuration of d-block elements?
B. $(n-1)d$ ... ns ...

ii. The ... of Mn in $KMnO_4$ is
C. +7

iii. Which ... following does not show variable valency?
B. Zn

iv. Which ... the following is paramagnetic?
D. All of above

v. The hybridization of Cu in $[Cu(NH_3)_4]^{2+}$ is
B. dsp ...

vi. Group VI B of transition elements contain
C. Cr, Mo, W

vii. The transition elements and their compounds are coloured due to splitting in
A. d-orbitals

viii. The first transition series ends on the element
C. Zinc

ix. The oxidation state of Fe in $K_4[Fe(CN)_6]$ is
A. +3 B. +2 C. +1 D. +4

x. The shape of $[Co(NH_3)_6]$ ... is
B. Octahedral

xi. The strength of binding energy of transition elements depends upon
B. number of unpaired electron

xii. If we add HNO_3 to the original vanadium (II) solution it produces
A. blue ions

xiii. All chromates are mostly
B. Yellow

xiv. The oxidation of CH_3OH is carried out with which of the following catalysts
D. $ZnO-Cr_2O_3$

xv. Acidified $KMnO_4$ acts as
B. Oxidizing agent

xvi. Brass alloy contains which of the following elements
B. Cu, Zn

xvii. Iron is used as a catalyst in
A. ... B. ... C. Haber Process

SUBJECTIVE

Time: 2.35 Hours Total Marks Section B and C: 65

Section - B Marks 42 (14 × 3 = 42)

Q2 Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

(i) a. What is Paramagnetism
b. What is the cause of Paramagnetism

(ii) a. How does vanadium ... be ...
c. Give confirmatory test for Fe^{+3} ions

(iii) Name the following co-ordination compounds
a. $K_4[Fe(CN)_6]$ b. ...

(iv) a. What are Complexes
b. Write the systematic name of the complex K_2PtCl_6.
c. Why Fe^{2+} ions do not exist in solution?

(v) a. How is chromate ion (CrO_4^{2-}) converted into dichromate on ...

(vi) a. Draw the geometric shape of co-ordination number 4 complexes
b. Why transition elements shows variable oxidation state?

4) In which titration end [illegible] 03

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

Q.3 a. How does ammonia react with [illegible] 04
b. When copper ion reacts with carbonate [illegible] 03
c. What are the use of potassium permanganate in [illegible] 06

Q.4 a. How does hexaaquamanganese(II) reacts with the following? 04
(i) hydroxide ions (ii) ammonia solution
b. What is geometry of the following complexes/compounds? 06
(i) $[MnCl_4]^{2-}$ (iii) $[Cu(NH_3)_4]^{2+}$ (iv) $[Co(NH_3)_6]^{3+}$
c. How does iron acts as a catalyst in the reaction between persulphate ions and iodide ions? 03

Q.5 a. Explain catalytic Activity of transition elements 04
b. What is a ligand? What are its types 04
c. Write IUPAC names of the following 05
(i) $K_4[Fe(CN)_6]$ (ii) $[Pt\,Cl_2\,(NH_3)_4]SO_4$ (iii) $[Cr\,(OH)_3\,(H_2O)_3]$
(iv) $[Co(NH_3)_6]Cl_3$ (v) $[Fe(H_2O)_6]^{3+}$

ORGANIC COMPOUNDS

Exercise Q3 (i) What are the main sources of organic compounds?

SOURCES OF ORGANIC COMPOUNDS

Fossil Fuels

The dead remains of living organisms are called fossil remains

The main sources of organic compounds are coal, petroleum [illegible] because they are formed from [illegible]

(i) COAL

- Coal is the major source of organic compounds
- It yields coke and coal-tar on pyrolysis or destructive distillation
- More than 200 organic compounds have been directly isolated from [illegible]
- These coal tar products form the starting materials for the [illegible]

2) PETROLEUM

- [illegible] is called
- [illegible] its place of

[illegible] ne ($CH_3CH=CH_2$ [illegible]

3) NATURAL GAS

- [illegible]
- [illegible]
- [illegible] organic matter
- [illegible]

4) PLANTS

[illegible] suitable methods of [illegible]

Examples

[illegible] fats and oils [illegible] compounds, vitamins [illegible]

PARTIAL AND TOTAL SYNTHESIS

The process in which compounds isolated from natural sources (e.g. plant material or coal or petroleum etc.) are used as starting materials to produce other organic molecules is called partial synthesis.

The process in which an organic molecule is synthesized from small and cheap readily available molecules is called total synthesis.

- [illegible]
- [illegible]

Examples

- Many synthetic organic compounds have replaced the compounds from natural sources e.g. [illegible] rubber, fibers, plastics, drugs, vita[illegible]
- In many cases the synthetic materials are superior to the natural compounds replaced e.g., synthetic dyes are superior to those of natural [illegible]
- In other cases the synthetic material are [illegible] from any other source e.g., ether, glycol, mercurochrome, aspirin, and the sulpha [illegible]

FERMENTATION

Fermentation is defined as the production of chemicals by the action of micro organism.

By employing appropriate organism hosts, useful substances are produced [illegible] vitamins and antibiotics.

QUICK QUIZ-1

(1) Define modern definition of organic chemistry?

Organic chemistry is that branch of chemistry which deals with the study of compounds [illegible]

[illegible]

2. Enlist ... organic compounds

3) Write important products from petroleum

Toluene $C_6H_5CH_3$ Xylene $C_6H_4(CH_3)_2$

4. What are alkaloids

e.g.

(5) Define fermentation?

Fermentation is ... the production of chemicals by the action of ...

By employing appropriate ... hosts, useful substances are produced ... vitamins and antibiotics

COAL (AS A SOURCE OF ORGANIC COMPOUND)

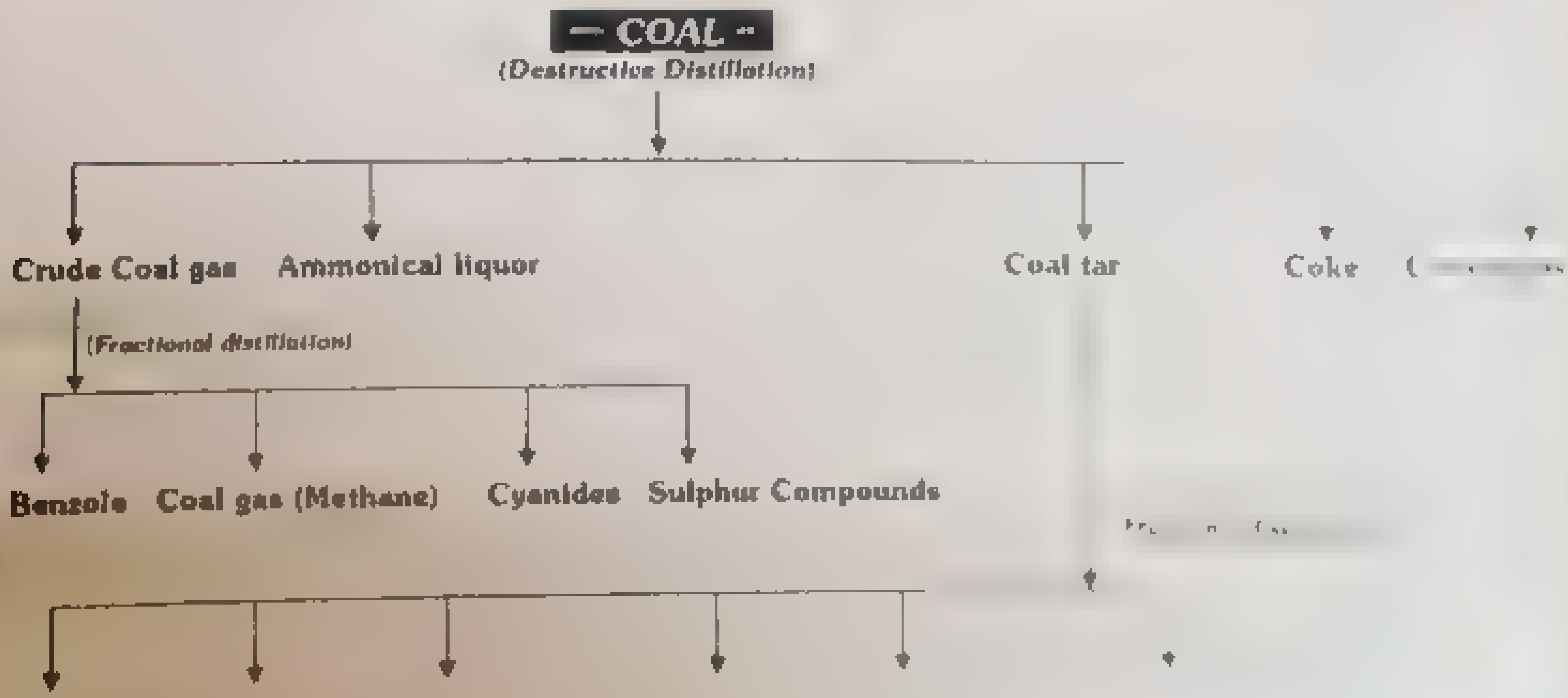
- Coal is produced by the decaying of trees buried under the earth ... temperature and pressure. These trees got converted into coal
- The total coal reserves of Pakistan are estimated by the geological survey of Pakistan ...

DESTRUCTIVE DISTILLATION OF COAL

The distillation carried out in the absence of air is called destructive distillation

Process

- When coal is heated in the absence of air (temperature range ...) ... coke coal gas and coal tar
- Coal tar contains a large number of organic compounds which separate out ... ***The separation of liquids on the basis of their boiling points is called fractional distillation***



CHARACTERISTICS OF ORGANIC COMPOUNDS

Exercise Q3 (ii) Write down the characteristics of organic compound from inorganic compounds

[illegible]

1. ***Composition***
   Carbon [illegible]

2. ***Combustion***
   Organic [illegible]

3. ***Melting and Boiling Points***
   Organic compound [illegible]

4. ***Solubility***
   Organic co[illegible] benzene, etc. [illegible]

5. ***Stability***
   Since organic comp[illegible] temperature into sim[illegible]

6. ***Electrical Conductivity***
   Due to the presence of covalent bonds, organic compounds are poor [illegible] both in fused state and in solution form.

7. ***Source***
   Most of organic compounds are obtained from [illegible]

8. ***Rate of Reaction***
   Their rates of reaction are very slow [illegible]

QUICK QUIZ-2

(1) What is coal?
It is a black colour mineral. Coal is produced by the [illegible] influence of temperature and pressure. These trees [illegible]

(2) What are the products of fractional distillation of coal tar?
Benzene, Toluene, Xylene, Naphthalene, Phenols and many ot[illegible]

(3) What we obtain by fractional distillation of coal gas?
Benzole, Coal gas (Methane), Cyanides, Sulphur Compounds

Exercise Q3 (iii) How organic compounds are used in our daily life?

USES OF ORGANIC COMPOUNDS

No field of science is so closely related with our daily activities as is organic chem[illegible]

- The food is mainly organic in nature.
- The food undergoes changes in our bodies which are organic chemical reactions.
- Metabolism, growth and maintenance of our bodily functions involve organic [illegible] case with all changes taking place throughout the entire living world, plant and anima[illegible]

1. *Food:*

2. Clothing

3. *Shelter:*

4. *Power and Transportation*

5. *Medicines and Drugs*

6. *Insecticides*

7. *Hormones and Steroids*

8. *Vitamins and Enzymes.*

9. *Antiseptics and Anesthetics*

10. *Pigments and Dyes*

11. *Paper and Inks.*

12. *Perfumes and Flavors.*

13. *Plastics, Rubbers, and Resins*

14. *Propellants and Explosives*

15. *Soaps and Detergents*

16. *Herbicides*

17. *Photographic films and Developers*

18. *Biological Problems and Organic Chemistry*

NEW ALLOTROPES OF CARBONS: BUCKY BALLS

- I
- I
- M
- Bucky

Structure of Bucky Balls

- These have carbon atoms ... cage like structure. They are called B...
- The simplest of them is C_{60} and its ...
- The carbon atoms fold are ...
- The new molec... hexagon structure

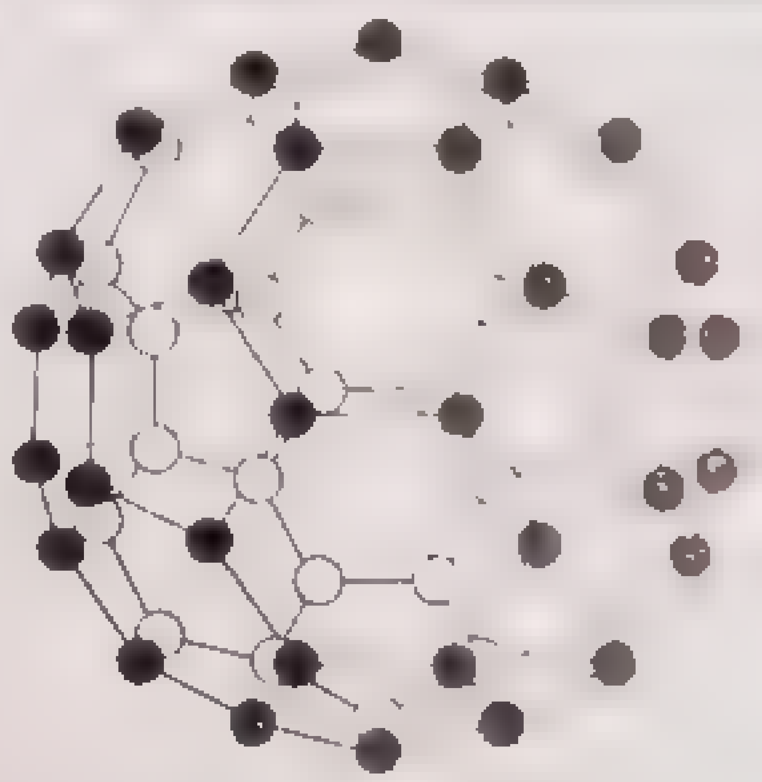


Fig Bucky Balls

QUICK QUIZ-3

(1) What are allotropes?

An element may exist in different crystalline forms. Th... is called allotropy

e.g. *(i)* C (as diamond) ______ in cubic form

(ii) C (as graphite) ______ in hexagonal form

(2) Define the third allotropic form of carbon.

- In 1985, a new group of allotropic forms of carbon was ...
- The full name of Bucky Balls is Buckminster Fullerenes
- Scientists named it after an architect Buckminster who de... Montreal

(3) Why it was given the name Bucky balls?

- Scientists named Bucky balls after an architect Buckminster who ... building in Montreal

FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

[illegible] importance of organic chemistry.

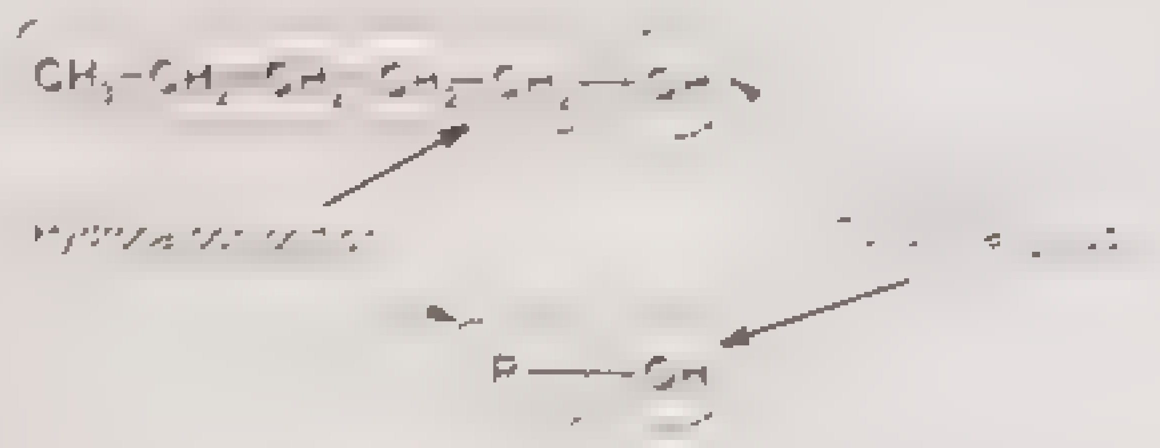
FUNCTIONAL GROUP

A functional [illegible] chemical properties.

- [illegible]
- [illegible]

Examples

Double bond [illegible]



R is defined as [illegible]

- The symbol R- is used [illegible] Thus R- can be CH_3- [illegible] valence by which the function[illegible]
- The functional group is the [illegible]
- Each functional group undergoe[illegible] molecule, it is possible to pred[illegible]

Importance:

The concept of functional group is importan[illegible]

(1) Functional groups serve as basis for nomencla[illegible]

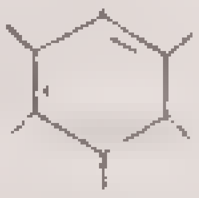
(2) Functional groups serve to classify organic com[illegible] same functional group belong to the same class

(3) A functional group is a site of chemical reactivity in a molecule. C[illegible] similar chemicals properties.

Remember! *Abbreviations for common Alkyl/Aryl groups. These are to be [illegible]*
*Methyl (**Me**), Ethyl (**Et**), n-Propyl (**n-Pr**), isopropyl (**iso-Pr**), [illegible] **Ph** [illegible]*

Following is the list of some common functional groups

Some functional groups

Family	Structure of functional group	[illegible]
Alkane	Containing only C – H and C – C single bond	
Alkene	$>C=C<$	
Alkyne	$-C\equiv C-$	
Arene		
Halide	$-\overset{\vert}{\underset{\vert}{C}}-\ddot{X}$ (X = F, Cl, Br, I)	
Alcohol	$-\overset{\vert}{\underset{\vert}{C}}-O-H$	
Ether	$-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	
Amine	$-\overset{\vert}{\underset{\vert}{C}}-N-H$, $-\overset{\vert}{\underset{\vert}{C}}-\underset{\underset{H}{\vert}}{N}-H$, $-\overset{\vert}{\underset{\vert}{C}}-\underset{\vert}{\ddot{N}}-$	
Nitrile	$-\overset{\vert}{\underset{\vert}{C}}-C\equiv N$	
Nitro	$-\overset{\vert}{\underset{\vert}{C}}-\overset{+}{N}\begin{smallmatrix}\nearrow O \\ \searrow O^{(-)}\end{smallmatrix}$	
Sulphide	$-\overset{\vert}{\underset{\vert}{C}}-S-\overset{\vert}{\underset{\vert}{C}}-$	
Sulphoxide	$-\overset{\vert}{\underset{\vert}{C}}-\overset{O^{(-)}}{\overset{\uparrow}{S}}-\overset{\vert}{\underset{\vert}{C}}-$	

II

[illegible]

HOMOLOGOUS SERIES

A homologous series ...

General Characteristics ...

(1) ...

(2) ...

(3) ...

(4) ...

(5) ...

(6) ...

QUICK QUIZ-4

(1) What are general formulas for alkanes, alkenes and alkynes?

...

(2) What are homologs?

A homologous ...

individual member ...

(3) Why we arrange compounds in homologous series?

The large number of ...

easier due to ...

- All compounds in the series ...
- All compounds in the series ...
- There is a gradual variation ...

Exercise Q3 (a) Give the chemical tests for the detection of elements in organic compounds

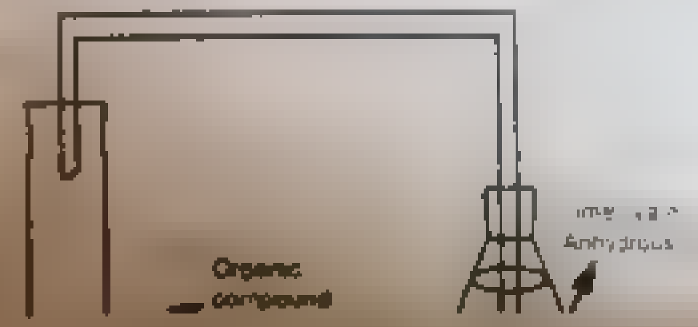
DETECTION OF ELEMENTS IN ORGANIC COMPOUNDS

- Carbon is an essential constituent of all organic compounds
- Hydrogen is also present in almost all organic compounds
- Some organic compounds may contain Nitrogen, Sulphur, and Halogen, Oxygen, Phosphorus and M...

(A) DETECTION OF CARBON AND HYDROGEN

Method

- A small amount of organic compound is heated with CuO in a glass test tube as shown in the figure
- On heating the mixture carbon and hydrogen are oxidized to CO_2 and H_2O respectively
- CO_2 turns lime water milky which proves the presence of carbon.
- The water vapors turn white anhydrous copper sulphate blue ...



Reactions

$$C + 2CuO \rightarrow CO_2 + 2Cu$$

$$\underset{\text{(Lime water)}}{CO_2 + Ca(OH)_2} \rightarrow \underset{\text{(Milkyness due to ppt. of CaCO}_3\text{)}}{CaCO_3} + H_2O$$

$$H_2 + CuO \rightarrow Cu + H_2O$$

$$\underset{\text{(White)}}{CuSO_4 + 5H_2O} \rightarrow \underset{\text{(Blue)}}{CuSO_4.5H_2O}$$

(B) DETECTION OF NITROGEN, SULPHUR AND HALOGENS

Preparation of Lassaigne's Solution Sodium Extract

(1) Cut a small piece of sodium metal with the help of knife
(2) Put this piece of sodium metal in a fusion tube
(3) Head the fusion tube in a flame to melt sodium meta.
(4) When [illegible] metal is melted, then add a small amount of powdered organic compounds into fusion tube
(5) Then heat fusion tu[illegible] red hot
(6) Break [illegible] 20cm³ of distilled water
(7) Mixed, boil a[illegible]
(8) The filtrate obtained is [illegible] solution or sodium extract
(9) Divide this filtr[illegible] test the presence of N, S ad (X) halogens respectively

Reactions (Chemistry of Preparation of Lassaigne's solution):

$$Na + C + N \rightarrow NaCN$$

$$2Na + S \rightarrow Na_2S$$

$$Na + X + C + N \rightarrow NaSCN$$

$$Na + X \rightarrow NaX$$

where X [illegible] Cl, Br, I

The tests for nitrogen, sulp[illegible]ogens are performed with Lassaigne's filtrate

TEST FOR NITROGEN.

Method

- To one portion of Lassaigne's filtrate a few drops of NaOH is added to make it alkaline and then then freshly prepared ferrous sulphate ($FeSO_4$) solution is added to it
- The solution is boiled and a few drops of $FeCl_3$ solution and HCl are added to it
- The appearance of blue or greenish blue (Prussian blue) color or ppt. proves the presence of nitrogen in the organic compound

Reactions

$$Na + C + N \rightarrow NaCN$$

$$FeSO_4 + 6NaCN \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \rightarrow \underset{\text{(Prussian blue color)}}{Fe_4[Fe(CN)_6]} + 12NaCl$$

Note:

- If a blood red color is produced instead of Prussian blue color then it proves that [illegible] are present in the organic compound

$$Na + S + C + N \rightarrow NaSCN$$

$$FeSO_4 + 6NaSCN \rightarrow Na_4[Fe(SCN)_6] + Na_2SO_4$$

$$4FeCl_3 + 3Na_4[Fe(CN)_6] \rightarrow \underset{\text{(Blood red color)}}{Fe_4[Fe(CN)_6]} + 12NaCl$$

TEST FOR SULPHUR

Method

- Acidify ...

Reactions

$$S^{2-} + 2CH_3COOH \rightarrow ...$$

$$H_2S + 2CH_3COO^- + Pb ...$$

TEST FOR HALOGENS

(i) Sodium Test

(C) DETECTION OF OXYGEN

- There ...
- Its pres...

Test 1

Test 2

- The second ... (OH), carbonyl (CO) ...
- If any of these ...

Test 3

- The sure test for o... the given compound ...
- If the sum of these per... thus confirms

(D) DETECTION OF PHOSPHORUS

- The solid substance is heated strongly ... mixture of sodium carbonate and ...
- The phosphorus present in the substance ...
- The residue is extracted with water, boiled with ...
- Then a hot solution of ammonium molybdate is added to it in ex...
- A yellow coloration of precipitate indicated the presence of phosph...

(E) DETECTION OF METALS

- The substance is strongly heated in a crucible preferably of platinum, till all res...
- An incombustible residue indicated the presence of a metal in the substance
- The residue is extracted with dilute acid and the solution is test for the presence of metallic radical by the usual scheme employed for inorganic salts

SOCIETY, TECHNOLOGY AND SCIENCE

ORGANIC COMPOUNDS FROM PLANTS AND ANIMALS

- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]

DRUGS FROM PLANTS

Quinine

[illegible]

Nicotine

[illegible]

Menthol

[illegible]

Camphor

[illegible]

Rutin

Used for th[illegible]

Hesperidin

Used for [illegible]

Curcumin

A choleretic obta[illegible]

Cocaine

A local anaes[illegible]

Caffeine

A CNS stimulant obtaine[illegible]

Bromelain

An anti-inflam[illegible]

EXERCISE

Q1: Select the right answer from the choices given with each question.

i. ...

ii. ...

iii. ...

iv. There are ...

v. ...

vi. Select ...

vii. ...

viii. When $AgNO_3$ ...

ix. When ...

x. The simplest ...

xi. If a molecule contains ...

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d) methane

(ii) Ans: (c) covalent bond

(iii) Ans: (d) Benzene

(iv) Ans: (c) Functional group

(v) Ans: (a) Pyridine

(vi) Ans: (c) CH_3-CH_2-OH

(vii) Ans: (b) Sodium

It is because it is a very ...

(viii) Ans: (d) Deep Yellow

(ix) Ans: (b) Deep blue

Anhydrous $CuSO_4$ is white. When ... then blue in colour due to formation o...

(x) Ans: (c) 60

(xi) Ans: (b) Polyfunctional

By definition a compound with more than ... is called a polyfunctional compound.

(xii) Ans:

(xiii) Ans:

Q2: Give brief answers for the following questions.

What is functional group?

A functional group is an atom or group of atoms in a molecule that g... chemical properties.

A molecule can contains more than one functional group. It is the ... Polyfunct... properties of each functional group may be modified by the presence of the others.

Examples: Double bond, triple bond, -Cl, -Br, -OH, $-NH_2$ groups etc.

(ii) **What is the difference between partial and total synthesis of organic compounds?**

The process in which compounds isolated from natural sources ... are used as starting materials to produce other organic molecules is called partial synthesis.

The process in which an organic molecule is synthesized from small and simple ... is called total synthesis.

(iii) **How organic compounds are derived by fermentation process?**

Fermentation is defined as the production of chemicals by the action of micro-organism.
By employing appropriate organism hosts of useful substances are produced ... vitamins and antibiotics.

(iv) **What is coal? How is coal used as source of organic compounds?**

(v) **What is name of new allotropic form of carbon? Give its definition?**

In 1985 a new group of allotropic forms of carbon was discovered ... These have carbon atoms ranging from forty to hundred. The ... cage like structure. They are called Bucky Balls.

(vi) **What is Homologous series?**

A homologous series is a series of compound in which adjacent members differ by a CH_2 unit. The individual members are called Homolog.

Example:

Alcohol series. Its general formula is ROH or $C_nH_{2n+1}OH$

The homologous series of alcohols can be represented as

n	R	Formula
1	CH_3-	CH_3OH
2	CH_3CH_2-	CH_3CH_2OH

(vii) **How sulphur can be detected in organic compounds?**

- Lassigne's filtrate is prepared and acidified with acetic acid.
- The solution is boiled to expel H_2S gas.
- The H_2S gas turns lead acetate paper black that indicates the ...

Reactions

$$S^{2-} + 2CH_3COOH \rightarrow H_2S + 2CH_3COO^-$$

$$H_2S + 2CH_3COO^- + Pb^{2+} \rightarrow PbS + 2CH_3COOH$$

Q3. Give detailed answers for the following questions.

(i) **What are the main sources of organic compounds?**

See Page 110

(ii) **Write down the characteristics of organic compound from inorganic compounds**

See Page 113

(iii) **How organic compounds are used in our daily life?**

See Page 113

(iv) **Write down any ten functional groups of organic compounds? Give reasons for their ... organic chemistry.**

See Page 116

(v) **Give the chemical tests for the detection of elements in organic compounds**

See Page 119

Section - C

Note: **Attempt any TWO questions All questions carry equal marks. (2 ×13=26**

Q 3 a Define [illegible]
b Explain [illegible]
c What are [illegible]

Q 4 a [illegible]
b [illegible]
c Give names of [illegible] 13

Q. 5 a Difference between organic and inorganic compounds with examples
b How carbon can be detected in organic compounds
c Give test for the detection of metals [illegible]
d What [illegible]

* Alkyl Groups are electron donating.
* Tertiary [illegible] are more reactive
* The alcohol whose carbon which is stable, is more reactive.
* Tertiary carbon atom CH_3

CH_3 → [illegible]

pushes electron

CHAPTER # 16

HYDROCARBONS

Catenation

The ability of carbon atoms ...

Thus carbon has ...

Hydrocarbons

Organic compounds which contain ...

TYPES OF HYDROCARBONS

The hydrocarbons ...

HYDROCARBONS

Open Chain or Acyclic Hydrocarbons

Saturated Hydrocarbons (Alkanes) CH_4 **(Methane)**

Alkenes ... **(Ethene)**

Alkynes ... **(Ethyne)**

OPEN CHAIN HYDROCARBONS

The hydrocarbons in which carbon atoms ... ***chain hydrocarbons***

TYPES OF OPEN CHAIN HYDROCARBONS

These are of two types

(1) Saturated hydrocarbons ...

(2) Unsaturated hydrocarbons ...

(1) SATURATED HYDROCARBONS

These are the hydrocarbons in which carbon atoms ...

- Each carbon atom is sp^3 hybridized ...
- These may have straight ... chain
- No further atoms or groups of atoms can be attached ... why they are called saturated hydrocarbons

Examples:

$CH_3-CH_2-CH_2-CH_2-CH_3$

n-Pentane (a straight chain alkane)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

2-Methylbutane (a branched chain alkane)

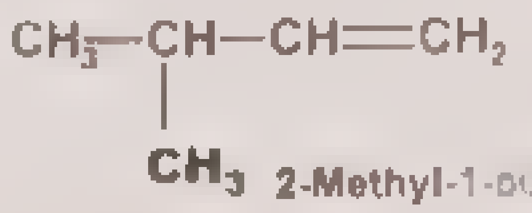
... in which at least two carbon atoms are attached through double ... alkenes and alkynes

... saturated hydrocarbons in which at least two carbon atoms are sp^2 hybrid... each other

- ... branched chain

$H_2C{=}CH-CH_2-CH_2-CH_3$

(straight chain alkene)



2-Methyl-1-bu...

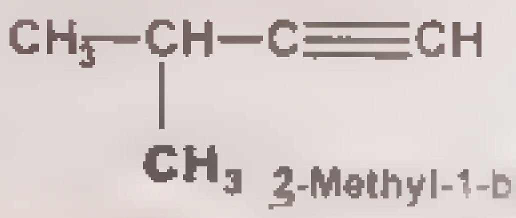
(ii) Alkynes or Acetylenes:

These are the unsaturated hydrocarbons in which at least two carbon atoms are sp h... a triple bond with each other.

- ... chain or branched chain

$CH{\equiv}C-CH_2-CH_2-CH_3$

(a straight chain alkyne)



2-Methyl-1-bu...

CLOSED CHAIN HYDROCARBONS:

These are the hydrocarbons in which carbon atoms attach with each other to form rings.

TYPES OF CLOSED CHAIN HYDROCARBONS:

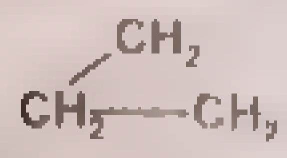
There are ... types

1. Alicyclic Hydrocarbons
2. Aromatic Hydrocarbons

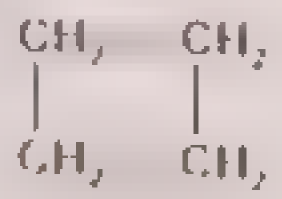
(1) ALICYCLIC HYDROCARBONS

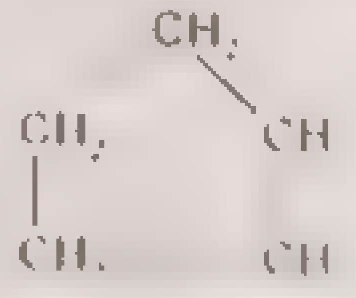
Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons

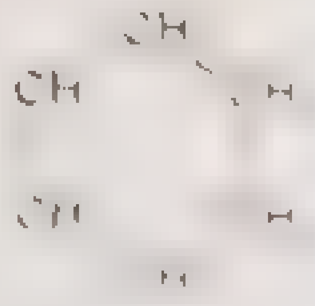
Alicyclic hydrocarbons possess two hydrogen atoms less than their ...

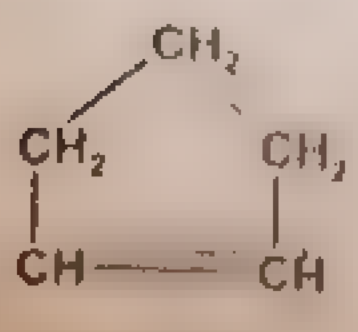


Cyclopropane

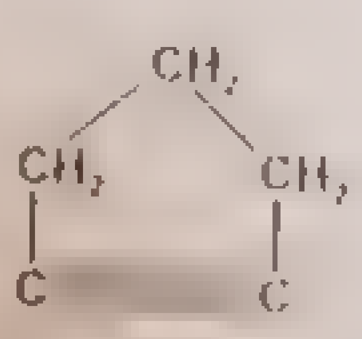


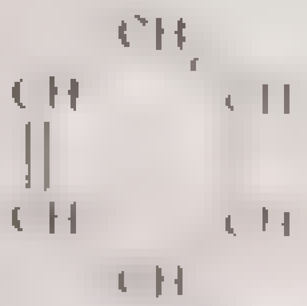






Cyclopentene

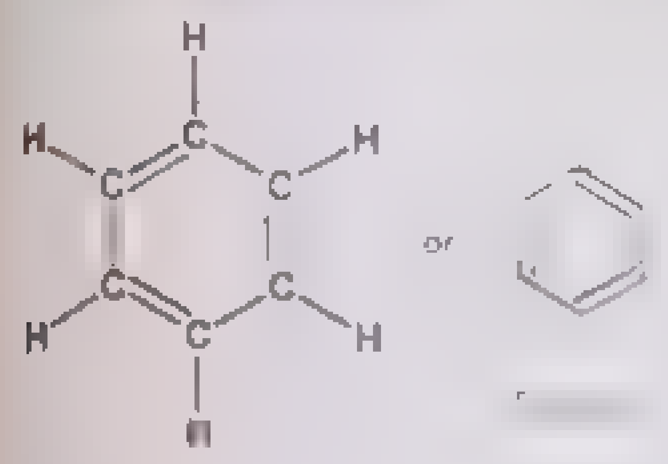


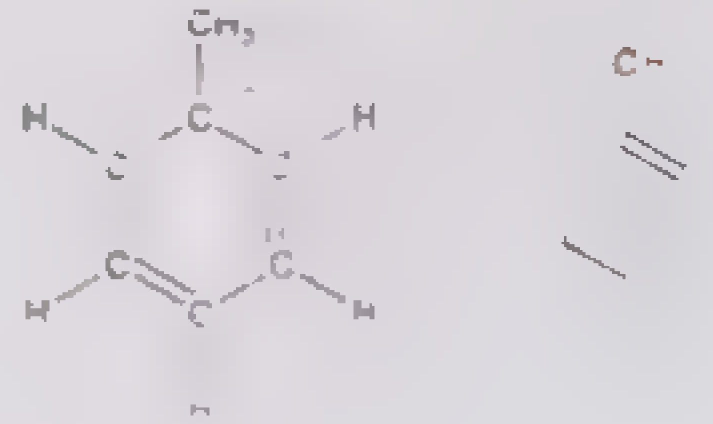


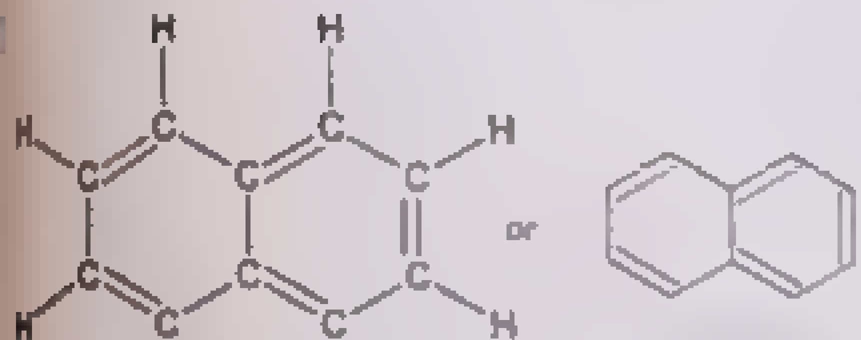
AROMATIC HYDROCARBONS

Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons

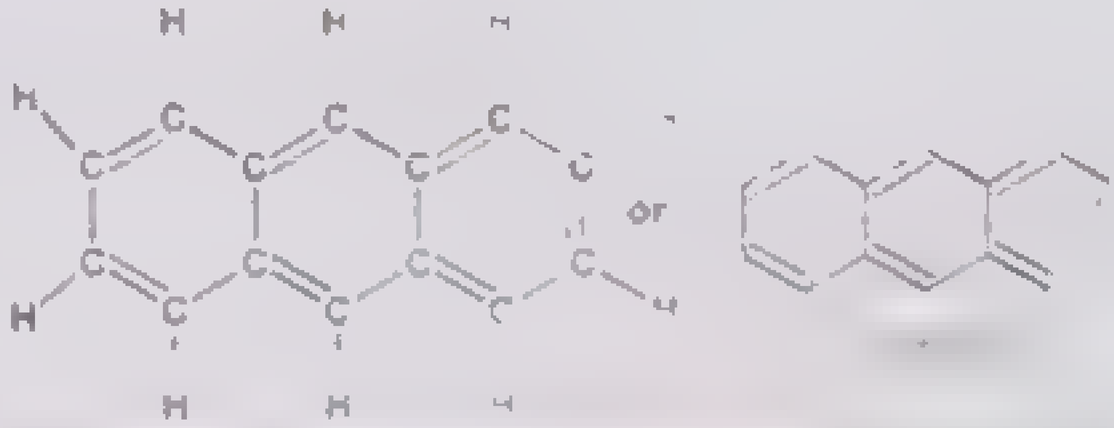
- In these ...
- Benzene is the ... and do ...







Naphthalene



QUICK QUIZ-1

1) What is catenation?

The ability of carbon atoms to attach with each other ...

Thus carbon has the ability to form long chains, multiple bonds and ...

e.g. $H_3C–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$ *(n-Octane)*

2) What are hydrocarbons?

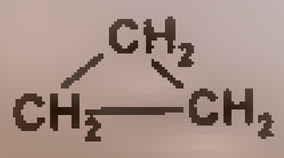
Organic compounds which contain carbon and hydrogen ...

These are of mainly two types

- *The hydrocarbons, in which carbon atoms attached ... chain hydrocarbons*

  e.g. $H_3C–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_3$ *(n-Octane)*

- *The hydrocarbons in which carbon atoms attach with each other ... hydrocarbons.*

  e.g. 

  Cyclopropane

3) Why saturated hydrocarbons are called paraffins

Aliphatic saturated hydrocarbons called alkanes are highly unreactive. Hence ...

(Latin *Parum* = little + *affins* = affinity) It means *little reactivity*

The unreactivity of alkanes is due to the inertness of a σ-bond and non-polar C–H ...

Examples: Methane, ethane etc

(4) Why unsaturated hydrocarbons are called olefins

Aliphatic unsaturated hydrocarbons having double bond are called Alkenes. These are also called olefins (Latin: *oleum*=oil+*facere*=to make). It means oil forming substances. This name was given because lower members of this class, **e.g.** ethene form oily liquids on reaction with Cl_2 gas.

(5) What is hybridization

The process in which atomic orbitals of different energy and shape [illegible] *set of equivalent orbitals of same energy and same shape is called hybridization.*

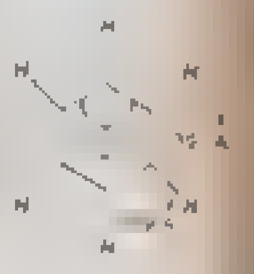
- The new orbitals formed are called hybrid orbitals.
- The concept of hybridization is used to explain number of valence, equivalent [illegible] etc of covalent molecules.
- There are various types of hybridization depending upon the [illegible] part in hybridization **e.g.**, sp^3, sp^2, sp, dsp^2, dsp^3, d^2sp^3 etc.

(6) Why benzene is called aromatic hydrocarbons

- The term aromatic is derived from Greek word aroma meaning fragrant.
- Initially this term was used for such compounds which contain less hydrogen to carbon ratio, shows high chemical stability and have characteristic smell. However, later on many stable compounds of this type were found odourless. Thus term 'aromatic' became associated with chemical stability of compound instead of odour.
- Since, benzene has low hydrogen to carbon ratio and shows high chemical stability, so it is called aromatic hydrocarbon.

(7) What is hexagonal structure?

A regular hexagonal structure has six equal faces and all angles of 120°.
e.g. benzene has hexagonal planar structure in which all carbon and hydrogen atoms are present in the same plane. All the angles are of 120^0. All C – C bond lengths are equal (1.397 Å). Similarly all C – H bond lengths are also equal (1.09Å).



ALKANES AND CYCLOALKANES

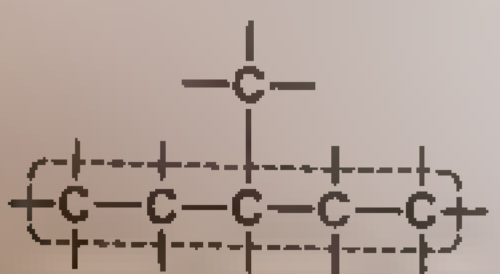
ALKANES

Acyclic saturated hydrocarbons are called alkanes

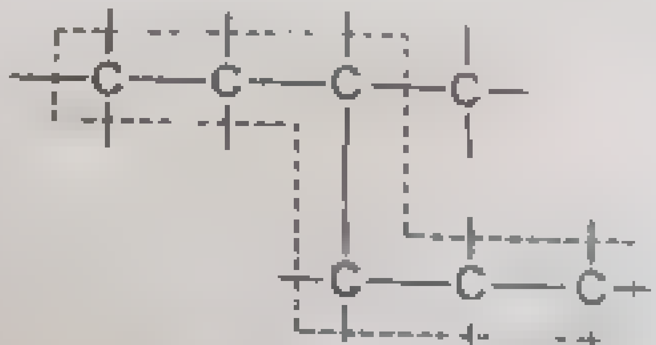
- These are simplest organic molecules with only C and H atoms.
- Their general formula is C_nH_{2n+2}
- These are commercially important as fuels and oils.

I.U.P.A.C. NOMENCLATURE OF ALKANES:

(1) Locate the largest continuous chain of carbon atoms independent of direction of the [illegible] called main chain, stem, principal chain or parent chain.

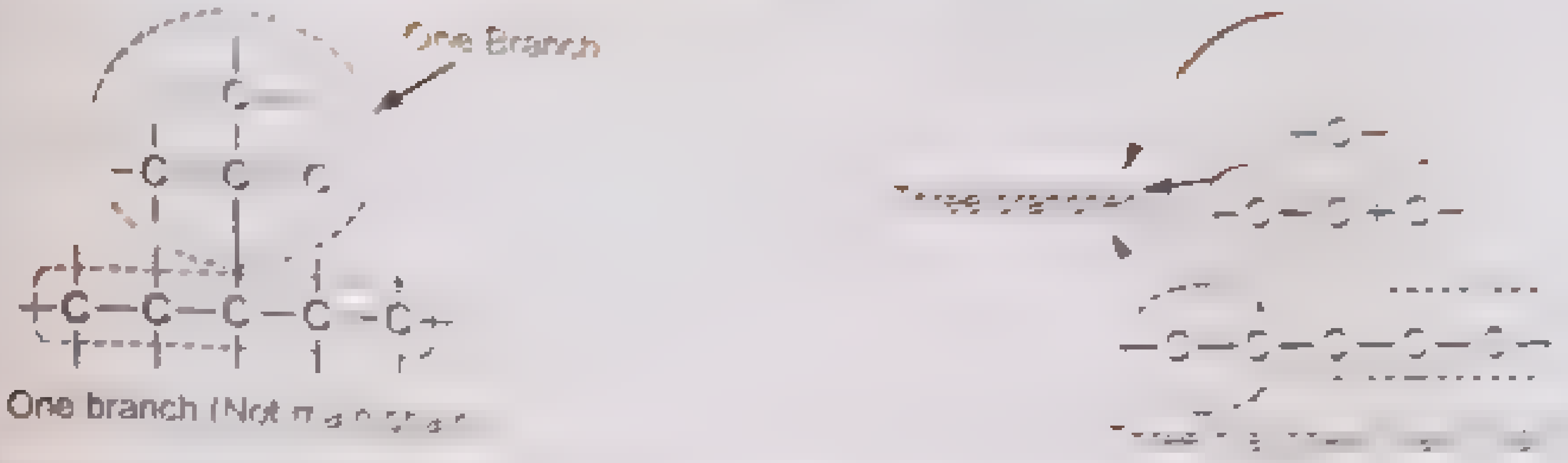


Longest chain (Horizontal)



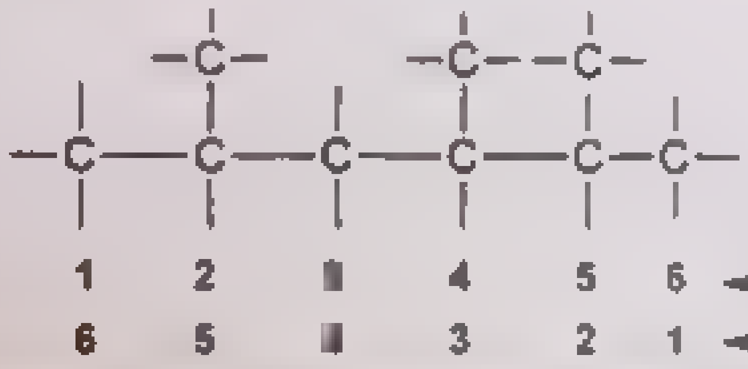
Longest Chain (Zig Zag)

(2) If there are two, ...
main chain ...



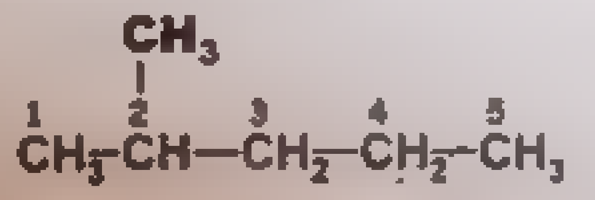
(3) Number the main chain start ...

(4) When two identical substituents are present at equal distance ...
with end which gives their minimum sum



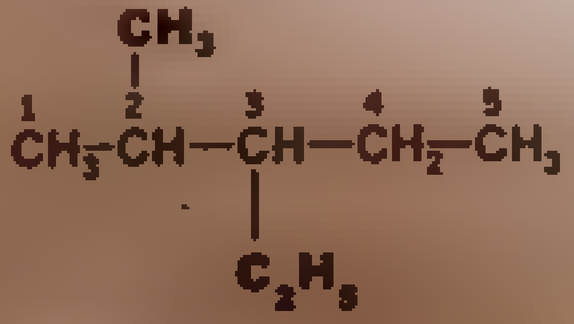
Since the sum of number 2+3+5=10, is less than 2+4+5=11 the correct ...

(5) The position of substituent is indicated by the number of C-atom ...
prefixed to the name of group separated by hyphen



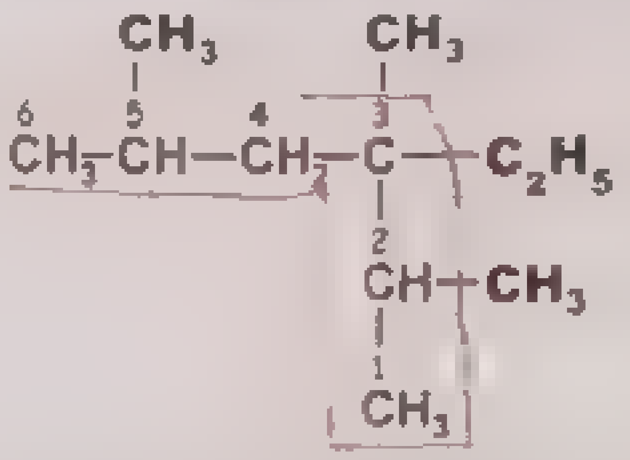
2-Methylpentane

(6) Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical ...
of increasing size, separated by hyphen.



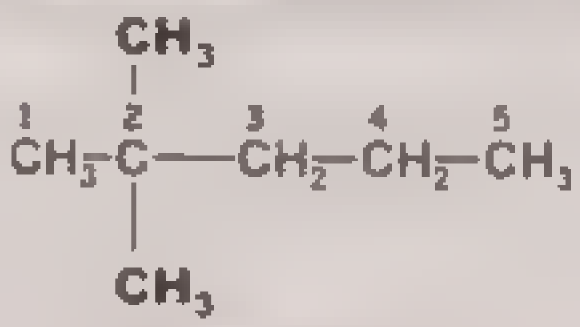
3-Ethyl-2-methylpentane

(7) When two or more like groups are present, their numbers are indicated by prefixes di, tri, tetra, etc. Their numbers are written together and are separated by commas.



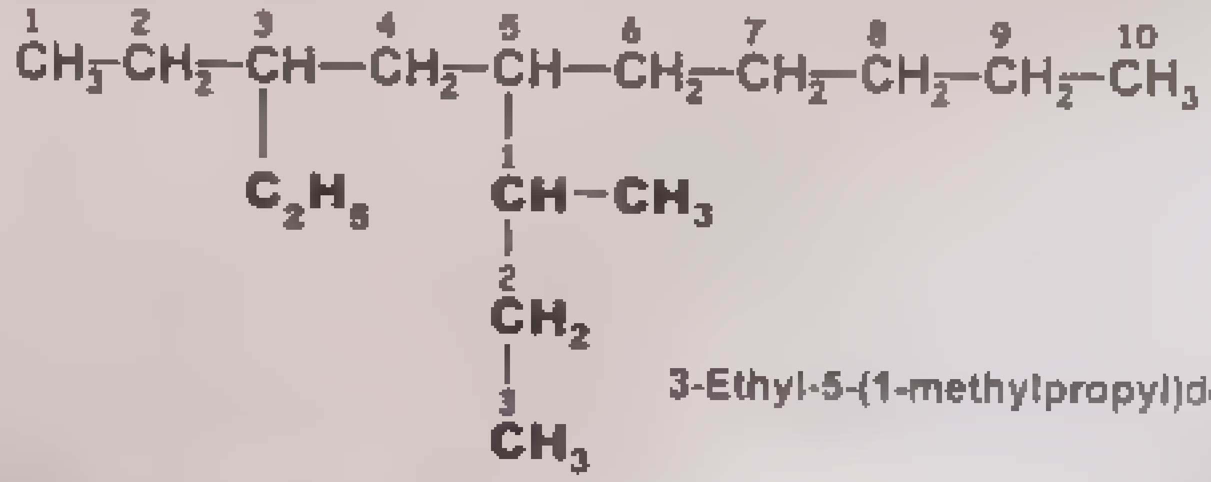
3-Ethyl-2,3,5-trimethylhexane

(8) If two identical groups appear at the same carbon, the number is repeated twice, separated by commas.



2,2-Dimethylpentane

(9) The longest chain of the substituent is numbered starting with the carbon attached directly to the main chain. Parentheses are used to separate the numbering of the substituent and the main chain.



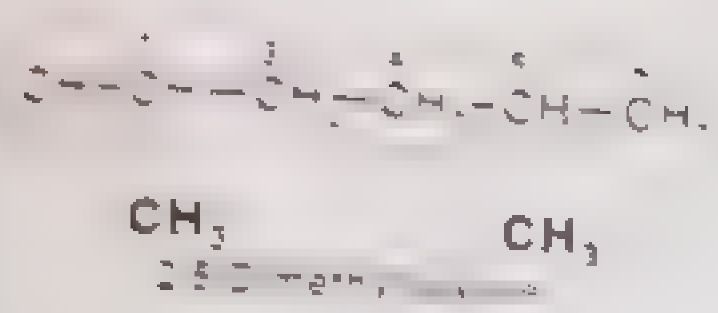
3-Ethyl-5-(1-methylpropyl)decane

The structural formula and names for the simple alkanes are shown in the following table.

Number of Carbon atoms	Formula		Line drawing	Alkane Name
1	CH_4 or		Not applicable (N.A)	Methane
2	C_2H_6 or	CH_3-CH_3		Ethane
3	C_3H_8 or	$CH_3-CH_2-CH_3$		Propane
4	C_4H_{10} or	$CH_3-(CH_2)_2-CH_3$		Butane
5	C_5H_{12} or	$CH_3-(CH_2)_3-CH_3$		Pentane
6	C_6H_{14} or	$CH_3-(CH_2)_4-CH_3$		Hexane
7	C_7H_{16} or	$CH_3-(CH_2)_5-CH_3$		Heptane
8	C_8H_{18} or	$CH_3-(CH_2)_6-CH_3$		Octane
9	C_9H_{20} or	$CH_3-(CH_2)_7-CH_3$		Nonane
10	$C_{10}H_{22}$ or	$CH_3-(CH_2)_8-CH_3$		Decane

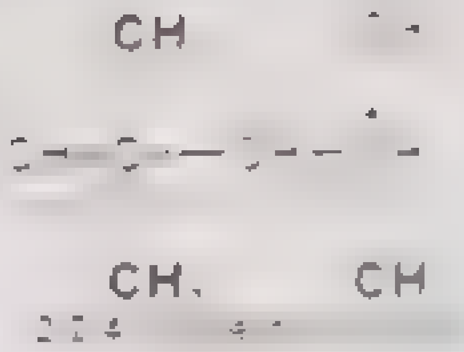
...TIVITY

(a)



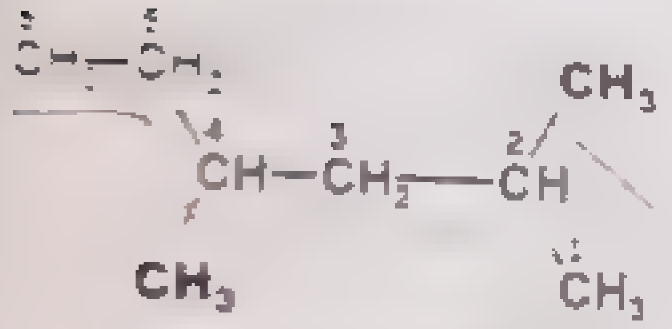
2,5-Dimethyl...

(b)



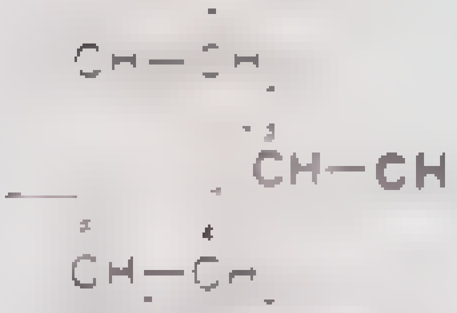
2,2,4-...

(c)



2,4-Dimethylhexane

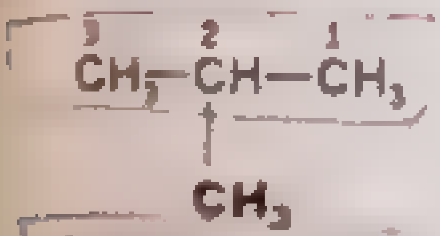
(d)



3-Meth...

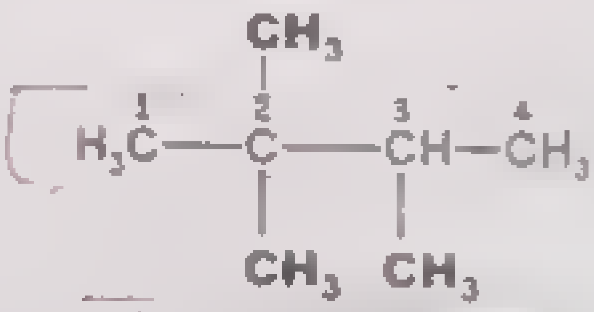
Indicate what is wrong with each of the following names. Give the correct IUPAC names if possible.

(a) 2-Dimethyl Propane



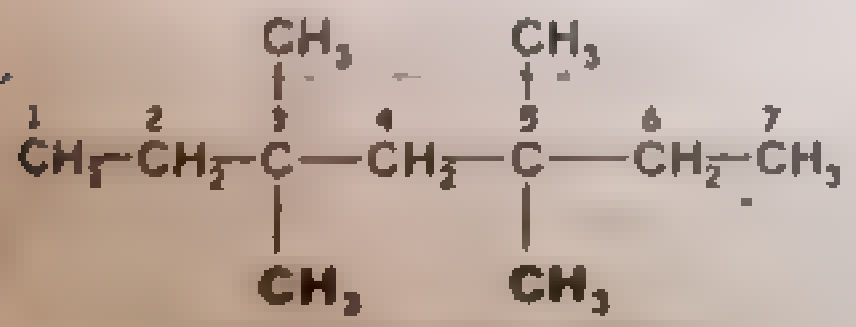
2-Methylpropane

(b) 2,2,3-Methyl Butane



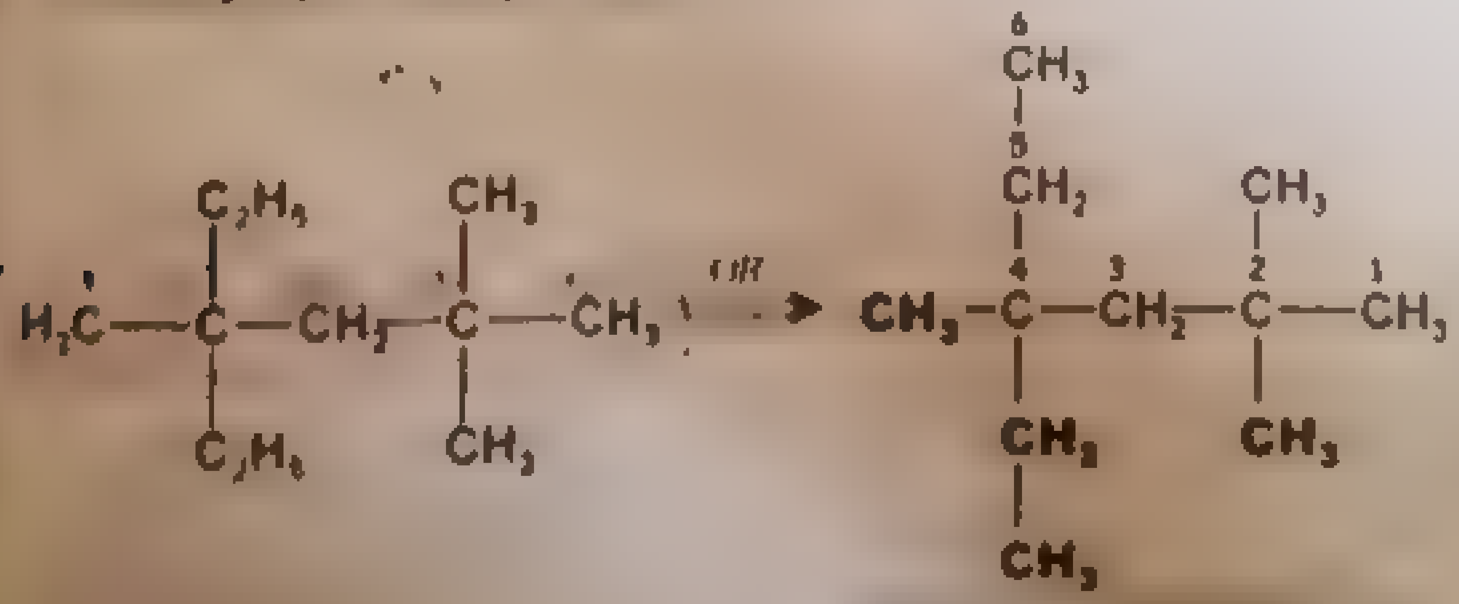
2,2,3-Trimethyl...

(c) 3,3-Dimethyl-5,5-Dimethyl Heptane

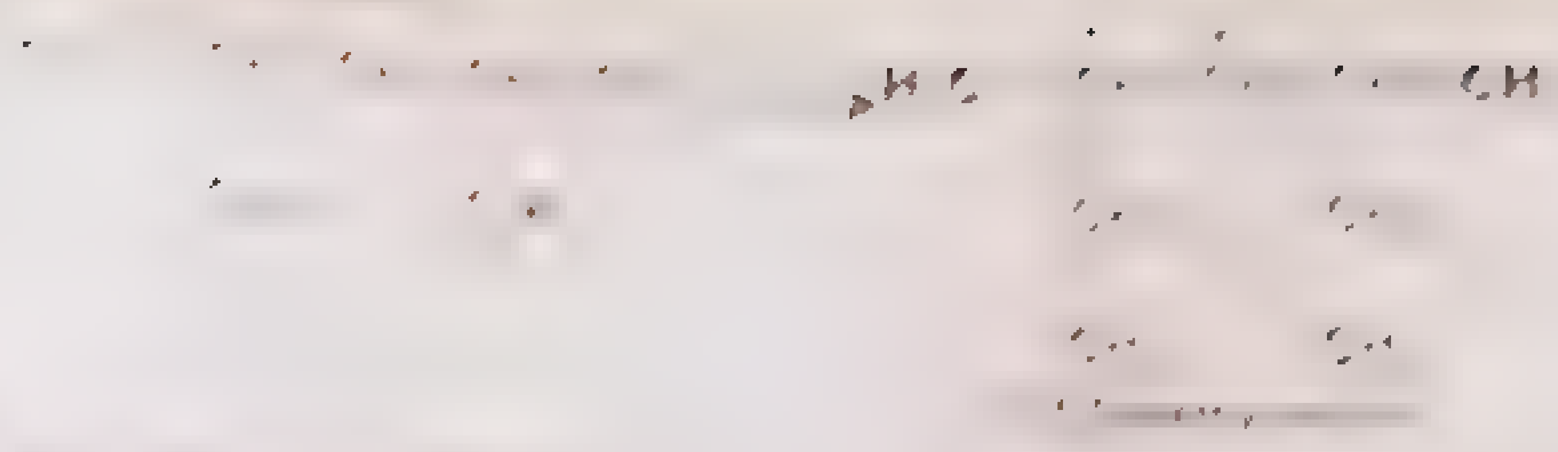


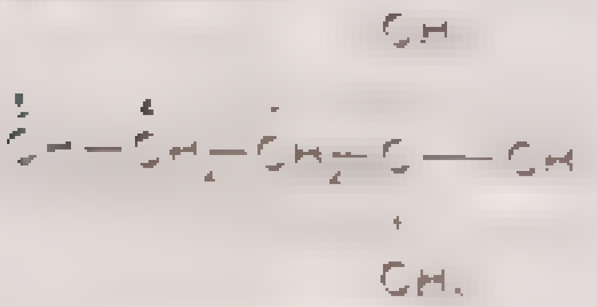
3,3,5,5-Tetramethylheptane

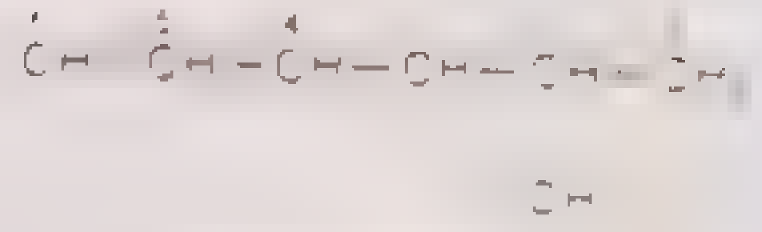
(d) 2,2-Diethyl-4,4-Dimethyl Pentane



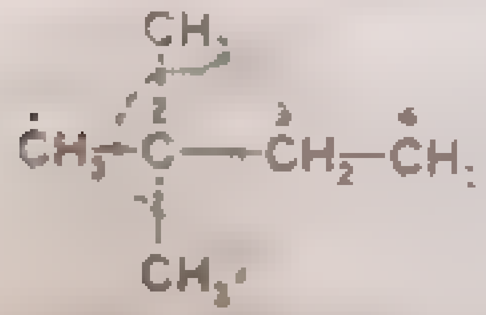
4 Ethyl-2,2,4-trimethylhexane





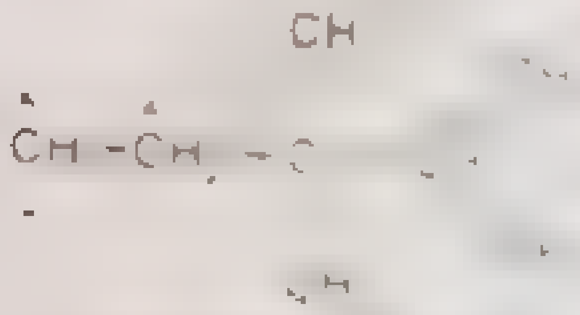


Trimethyl Ethyl Methane

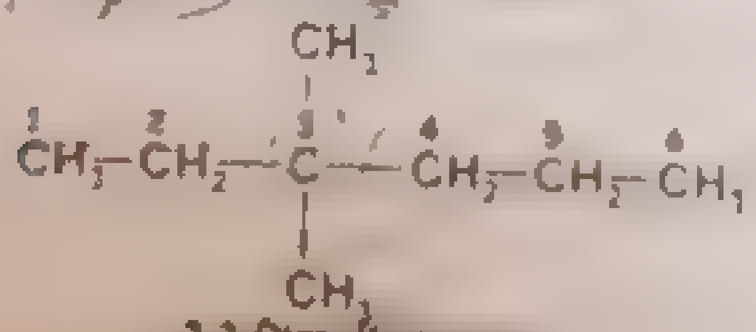


2,2-Dimethylbutane

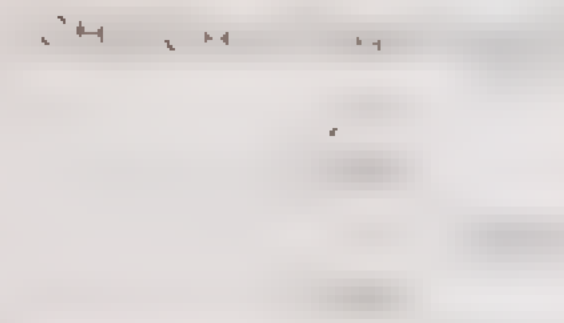
Dimethyl Ethyl Isopropyl M



(e) Dimethyl Propyl Ethyl Methane

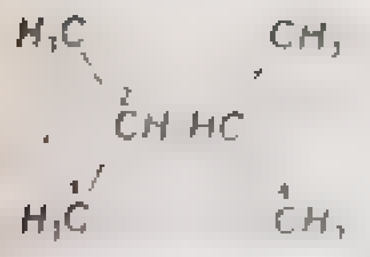


3,3-Dimethylhexane

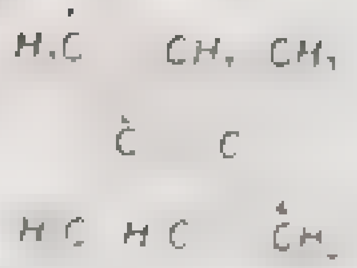


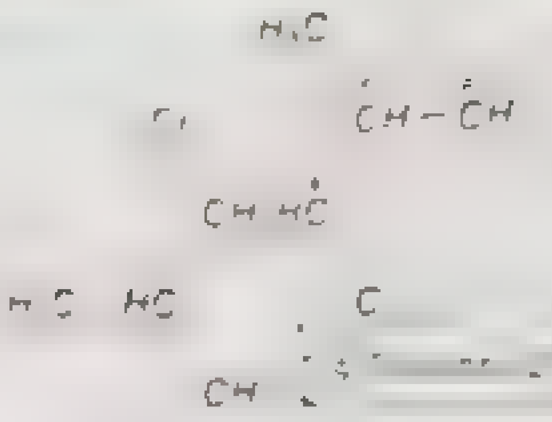
MORE PRACTICE

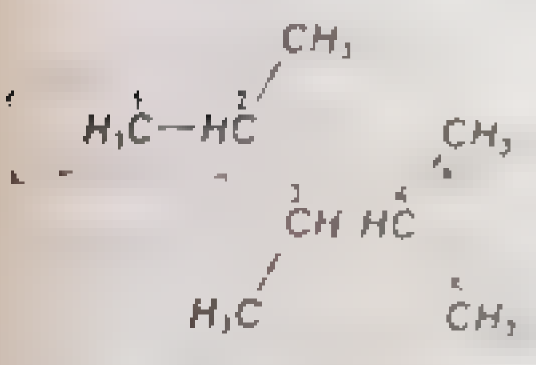
Alkanes



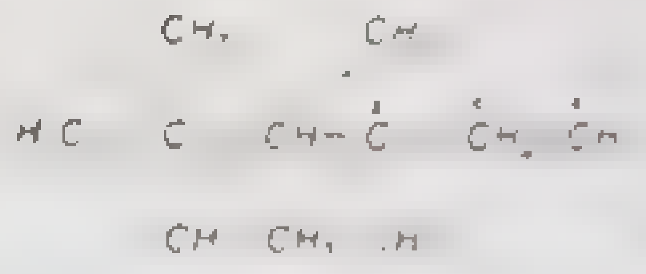
2,3-Dimethylbutane

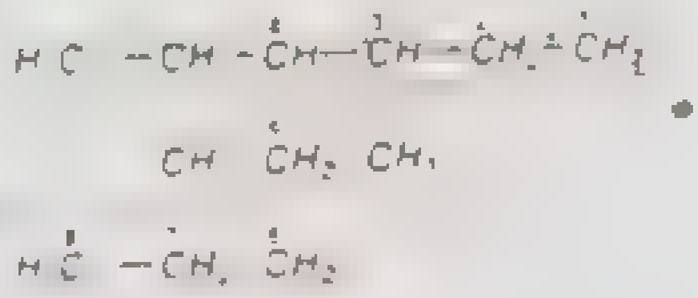


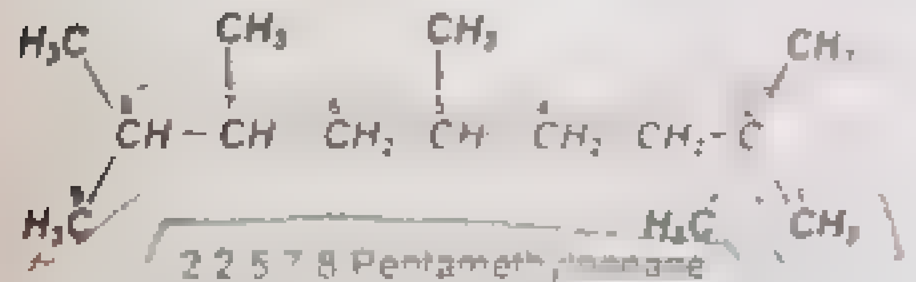




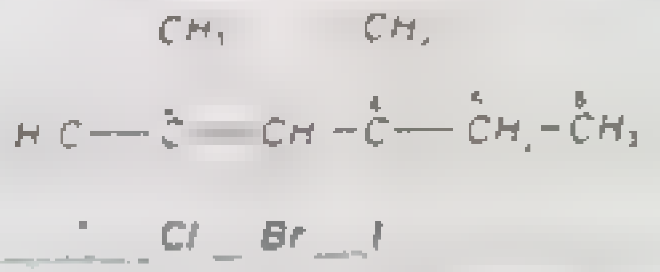
2,3,4-Trimethylpentane

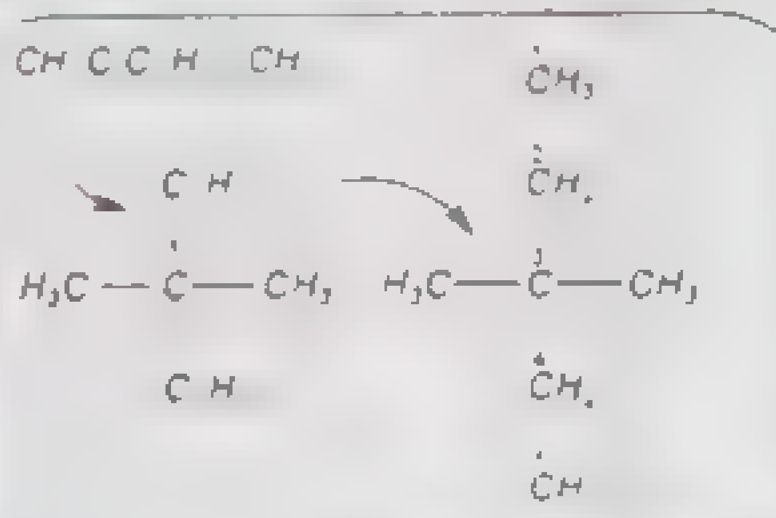




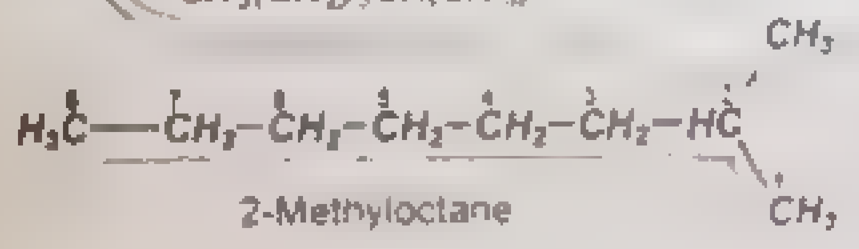


2,2,5,7,8-Pentamethylnonane



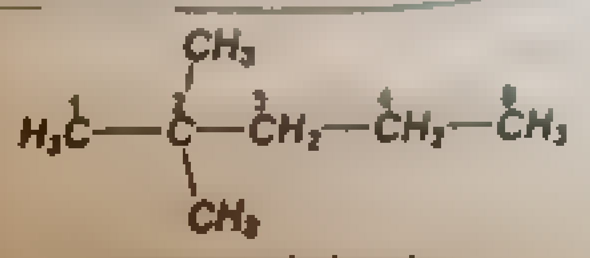


$CH_3(CH_2)_5CH(CH_3)_2$

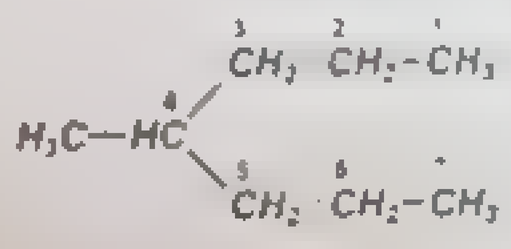


2-Methyloctane

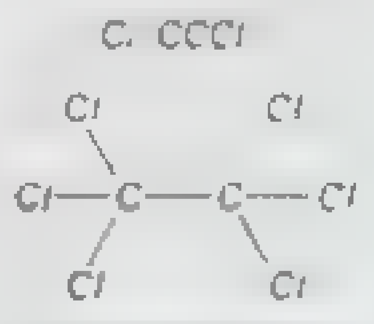
$CH_3C(CH_3)_2CH_2CH_2CH_3$



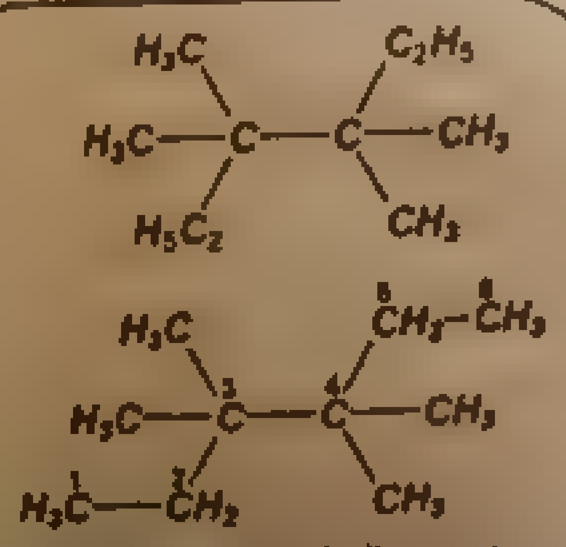
2,2-Dimethylpentane



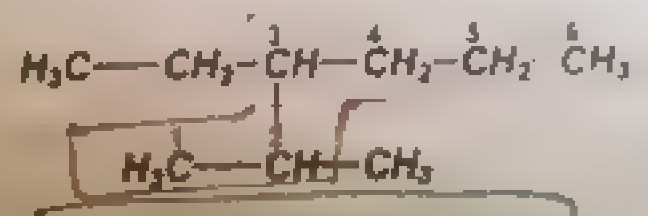
4-Methylheptane



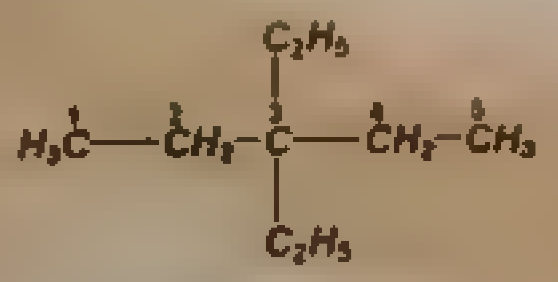
Hexachloroethane



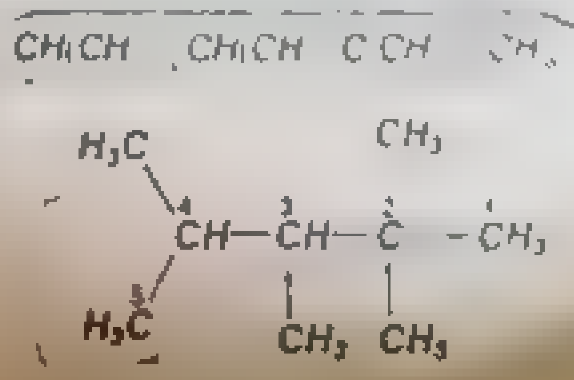
3,3,4,4-Tetramethylhexane



3-Ethyl-2-methylhexane



3,3-Diethylpentane



2,2,3,4-Tetramethylpentane

PHYSICAL PROPERTIES

QUICK NOTE

Effect of branching ...

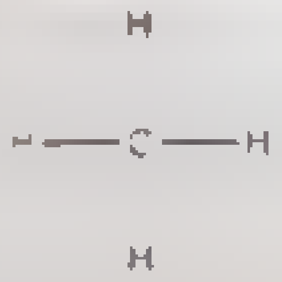
Effect of branching on boiling point of alkanes

STRUCTURE

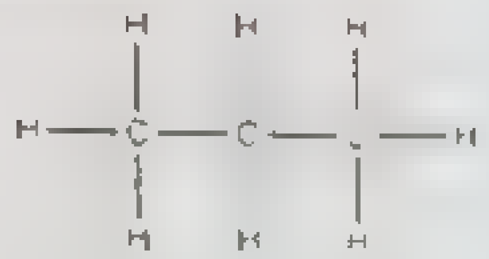
Normal Alkanes

- Alkanes are the s... σ bonds
- They have a ge... atoms present for a...
- Structures of the s...
- As the number of C at...

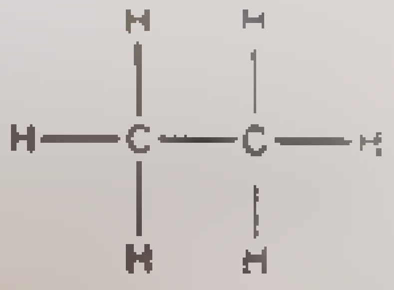
Methane CH_4 (b pt = -160°C)



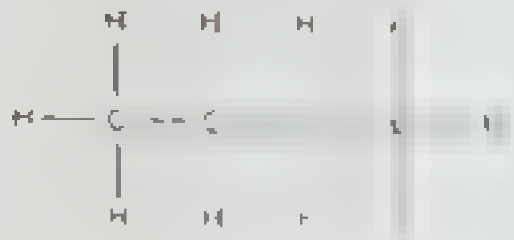
Propane C_3H_8 (b pt = -42°C)



Ethane C_2H_6 (b pt = -89°C)



Butane C_4H_{10} b pt = -0.4...



Isomeric Alkanes:

- The molecular formula for the C... to C... alkanes ...
- However for C_4H_{10} there are two possible constit...
- The isomers have different chemical physical properties ...

(iii) Non-polar Bonds:

- [illegible] electronegativities of carbon (2.5) and hydrogen (2.1) do not differ appreciably. Therefore, the bonding [illegible] C–H and C–C [illegible] bonds [illegible] polar. [illegible] reagents such as acids, alkalies, oxidizing agents, etc. find no place in the alkane molecules for reaction.
- However, under suitable condition, Alkanes give two types of reactions
  - (i) [illegible] Reactions
  - (ii) Substitution Reaction
- [illegible] high temperature [illegible] formation of highly reactive free radicals.

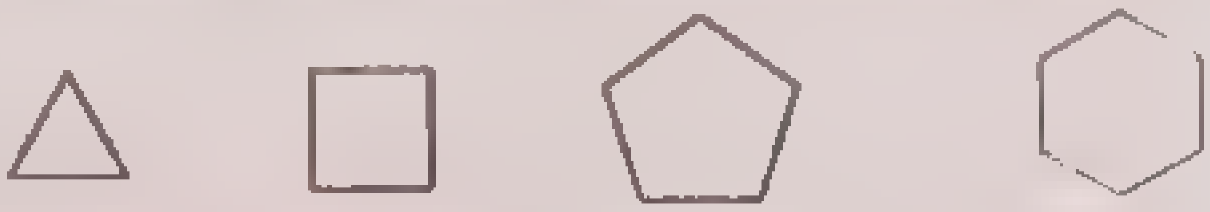
CYCLOALKANES

Another type of molecule containing only sp^3 hybridized C and H atoms connected by σ bonds is possible with ring of 3 or more C atoms. These are the cycloalkanes. These are both synthetic and natural.

NOMENCLATURE:

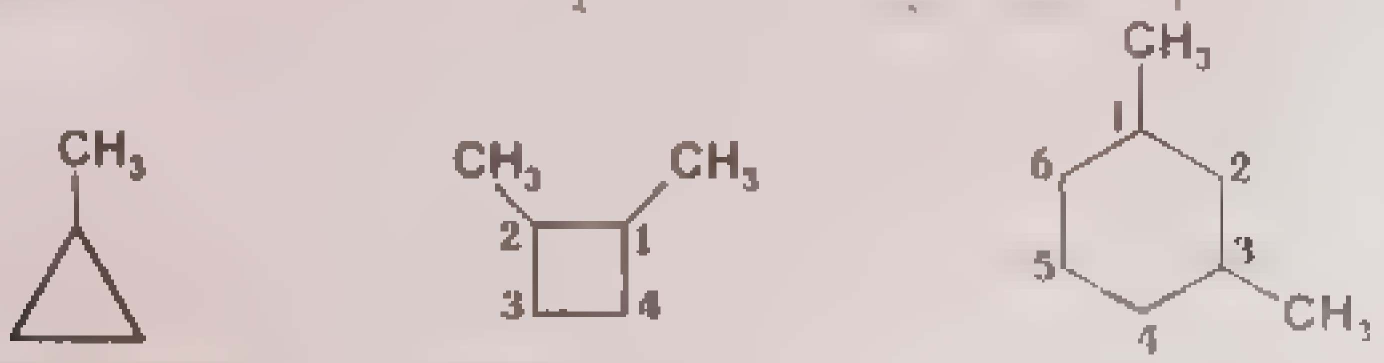
- According to IUPAC system, cycloalkanes with one ring are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.

Examples:



Cyclopropane Cyclobutane Cyclopentane Cyclohexane

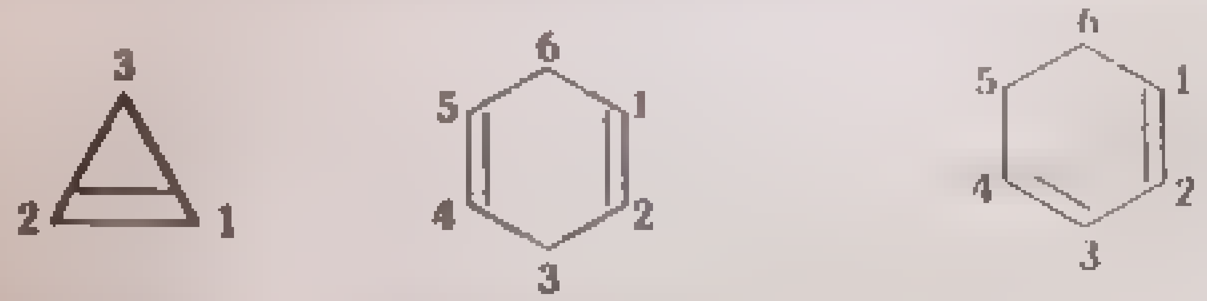
- The substituents are numbered in such a way that the sum of numbers is kept minimum, e.g.



Methylcyclopropane 1,2-Dimethylcyclobutane 1,3-Dimethylcyclohexane

- If the alicyclic hydrocarbon is unsaturated, the rules applied to [illegible] triple bond) are used. *Multiple bonds are given the lowest possible number.*

Examples:



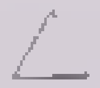
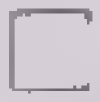
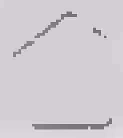
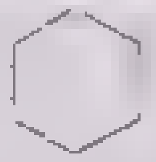
Cyclopropene Cyclohexa-1,4-diene Cyclohexa-1,3-diene

PHYSICAL PROPERTIES:

- Cycloalkanes have low polarity. Thus the only intermolecular forces [illegible] and the very weak induced dipole – induced dipole forces, also known as [illegible].
- These forces can be easily overcome. As a result, compared to other functional groups, [illegible] alkanes, cycloalkanes tend to have low melting and boiling points.

...UCTURE:

- They have a generic formula of C_nH_{2n}. Thus, these have two less H ato...
- These are isomers of alkenes.
- They have sp^3-hybridized carbon atoms

Cyclopropane	C_3H_6	
Cyclobutane	C_4H_8	
Cyclopentane	C_5H_{10}	
Cyclohexane	C_6H_{12}	

ACTIVITY:

- The reactivity is very similar to the closely related alkanes ...
- Since C and H atoms have very similar electronegativities, so ...
- As a result, cycloalkanes, like alkanes, are not a very reac...

...UICK QUIZ-2

What are polar, no-polar and weakly polar compounds?

Polar Compounds

The compounds in which electron density is unsymmetrical are called p...
In such compounds, electron density is more present on one side ... centers are developed within a molecule. **e.g.** water, methanol (CH_3OH)

Non-Polar Compounds

The compounds in which electron density is symmetrical are called non-po...
In such compounds, electrons density is uniformly distributed through... negative centers are not developed within a molecule **e.g.** carbon tetrachloride ...

Weakly

Polar Compounds

The compounds in which electron density is slightly unsymmetrical ...
In such compounds, electron density is slightly more present on one side tha... negative centers are developed within a molecule **e.g.** acetone etc

What are isomers?

The compounds having same molecular formula but different structures and p... the phenomenon is called isomerism

Example:

Ethanol and dimethyl ether are isomers of each other. Both have molecular formula ... structures and properties.

CH_3-CH_2-OH (Ethanol) CH_3-O-CH_3 (Dimethyl ether)

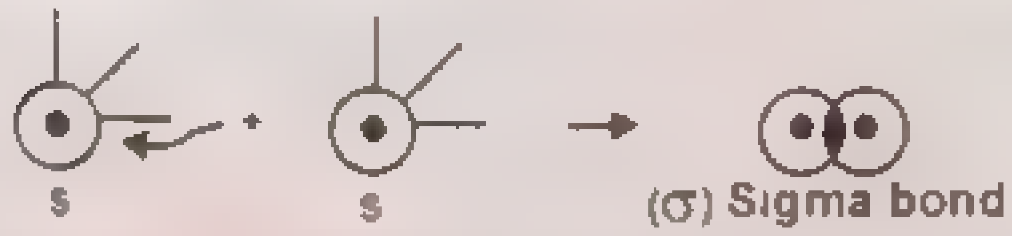
What are inert compounds?

The compounds which do not react under certain conditions are called inert compounds.

4 What is sigma bond?

[illegible]

Example



5 *What are intramolecular and intermolecualr forces?*

- [illegible]

  Examples

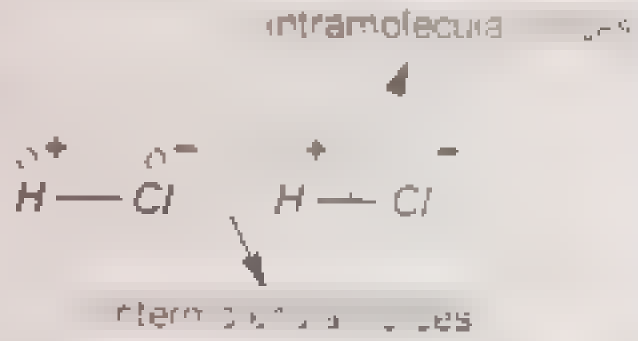
  [illegible]

- *The forces of attractions between atoms within a molecule are called intramolecular forces*

  Examples:

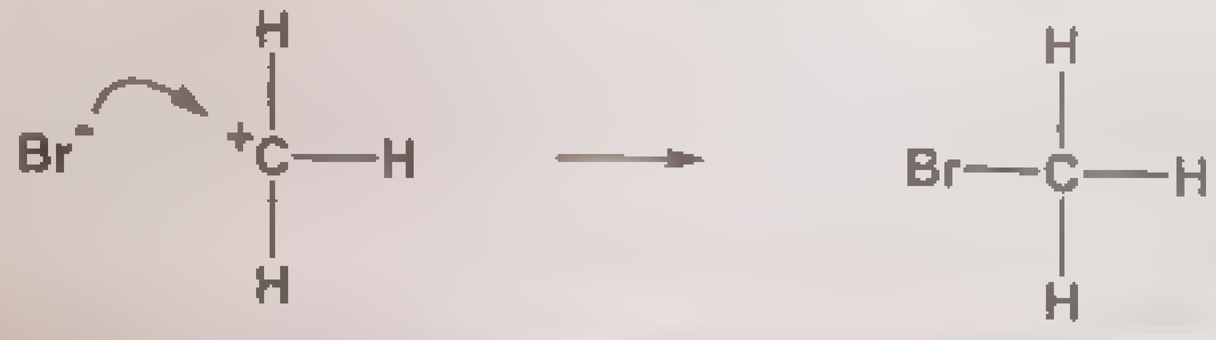
  Chemical bonds i.e. [illegible] bond, covalent bond, co-ordinate [illegible]

- *Intramolecular [illegible] stronger than intermolecular forces*



HOW TO DESCRIBE REACTION MECHANISM

- When reaction mechanisms are being described, a 'curly arrow' is sometimes used to show the [illegible] of a pair of electrons
- The beginning of the arrow shows where the electron pair starts from and the arrow head shows where the pair ends up. **e.g**



- The arrows show that a pair of electrons is moving from the Br [illegible] to the region between [illegible] the carbon. Thus a covalent bond is formed between the atoms
- The same reaction is shown again below, with all the bonding electrons indicated

A half arrow is used to show the movement of a [illegible] electron in [illegible] free radicals.
The beginning of the arrow shows where the [illegible] electron starts from and the half arrow head shows where it ends up e.g.,

$$H^{\bullet} \quad Cl{-}Cl \longrightarrow H{-}Cl \quad Cl^{\bullet}$$

It can be shown as

$$H^{\bullet} \quad Cl{-}Cl \longrightarrow H{-}Cl + Cl^{\bullet}$$

This is shown again [illegible]

$$H^{\bullet} \quad :\ddot{Cl}:\ddot{Cl}: \longrightarrow H{-}Cl + Cl^{\bullet}$$

[Sum]mary of the way curly arrows and half-arrows are used

(1) Curly arrows show the movement of [illegible]

Electron pair starts here ... ... finished here

(2) Curly half arrows show the movement of a single [illegible]

Electron pair starts here ... ... finished here

[RA]DICAL SUBSTITUTION REACTIONS

The substitution of hydrogen of an alkane molecule by a halogen atom takes place as [illegible]

$$-\overset{|}{\underset{|}{C}}-H + X{-}X \xrightarrow[\text{heat}]{\text{light or}} -\overset{|}{\underset{|}{C}}-X + HX$$

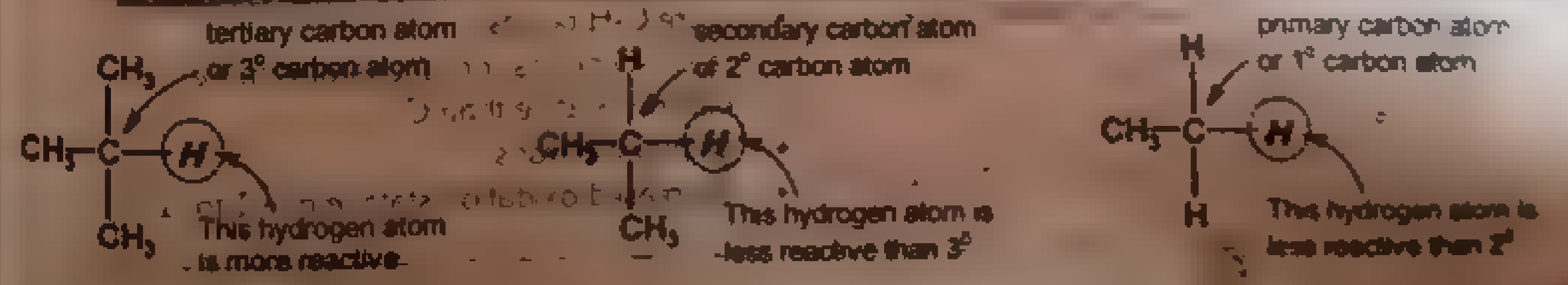
(X = Cl or Br)

[Im]portant to Note:

- Substitution of R-H by –X provides the alkyl halide, R-X and HX
- Alkane R-H relative reactivity order 3° > 2° > 1° > methyl.
- Halogen reactivity $F_2 > Cl_2 > Br_2 > I_2$.
- Only chlorination and bromination are useful in the laboratory.
- Reaction proceeds via a radical-chain mechanism [illegible]

Important!

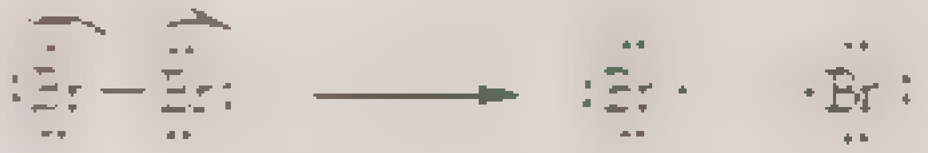
- 3° is [illegible] is attached [illegible]
- 2° is [illegible] is attached [illegible]
- 1° is [illegible] is attached to three [illegible]



REACTION MECHANISM *Radical chain mechanism for reaction of methane with Br*

Step 1 (Initiation)

The [illegible]

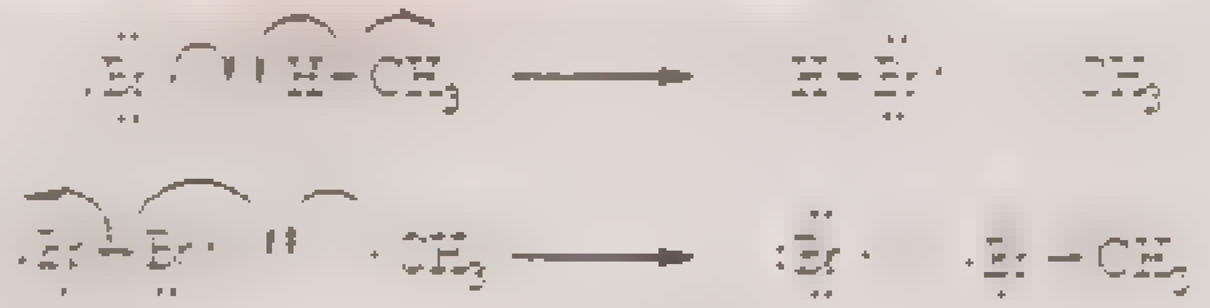


Step 2 (Propagation)

(a) A brom[illegible] from methane to form HBr [illegible]

(b) The me[illegible] atom from another molecule of Br_2 [illegible] product [illegible]

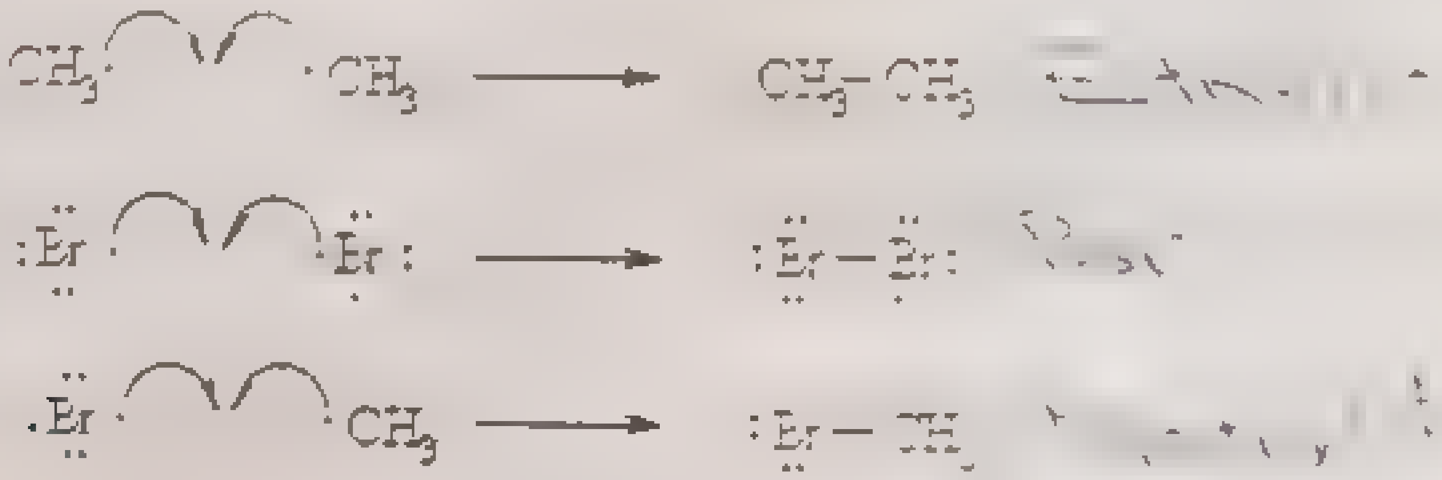
Both the [illegible] are repeated over and over again



Step 3 (Termination)

[illegible] ethane, Br_2 [illegible]

- These reac[illegible] the cycle



OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

- Oxidation (O) and reduction (R) are oppos[illegible] these reactions are called **redox reactions.**
- Organic chemists will normally describe a reac[illegible] the major organic component

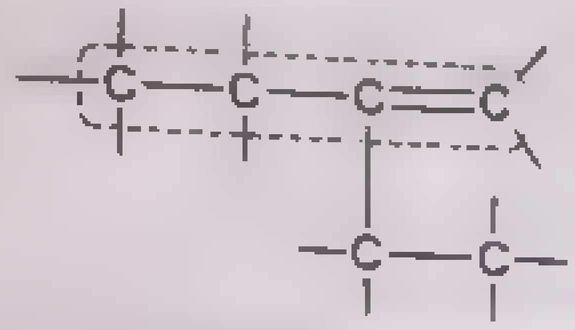
Oxidation	Reduction
• more C-O bonds (or other atoms more electronegative than C)	[illegible]
• less C-H bonds	[illegible]
• loss of electrons	[illegible]
• increased oxidation state, e.g. +1 to +3	[illegible]

ALKENES

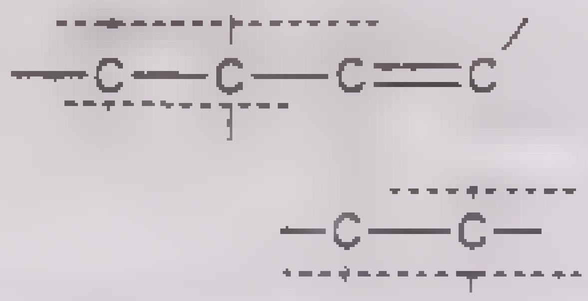
Acyclic unsaturated hydrocarbons containing double bond are called alkenes

NOMENCLATURE:

(1) The longest continuous chain [illegible]
(2) The ending '**ane**' is replaced by '**ene**'

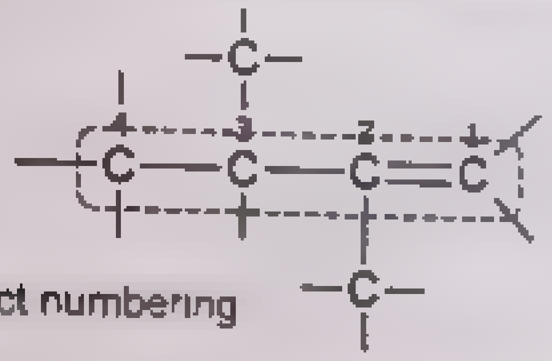


Longest Chain with double bond (Correct)

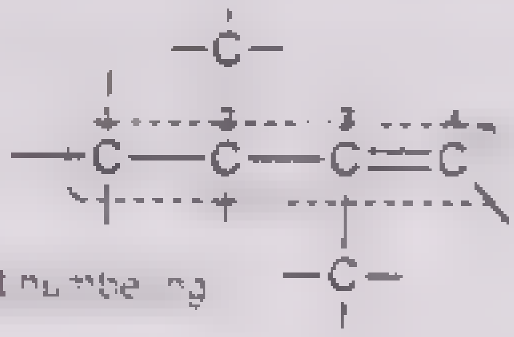


Longest Chain without double bond [illegible]

(3) The chain is numbered in such a manner as to give [illegible]

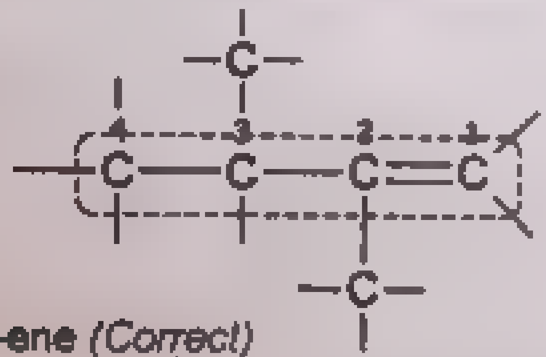


Correct numbering

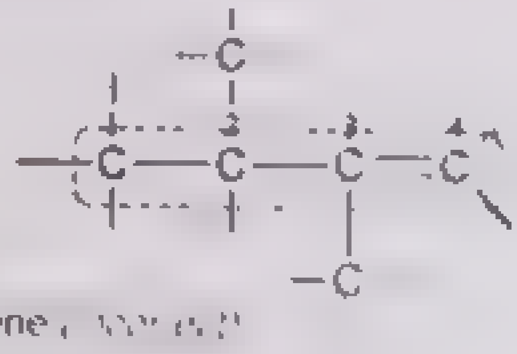


Incorrect numbering

(4) The position of double bond is indicated by the lower number of C-atom

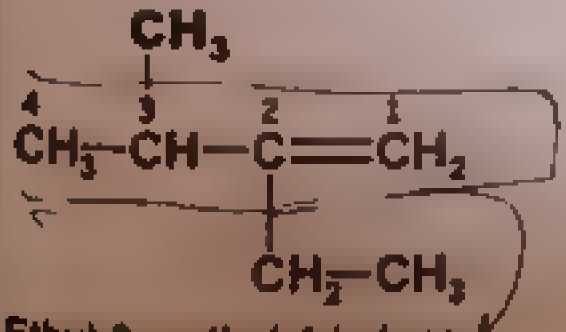


1-ene (*Correct*)

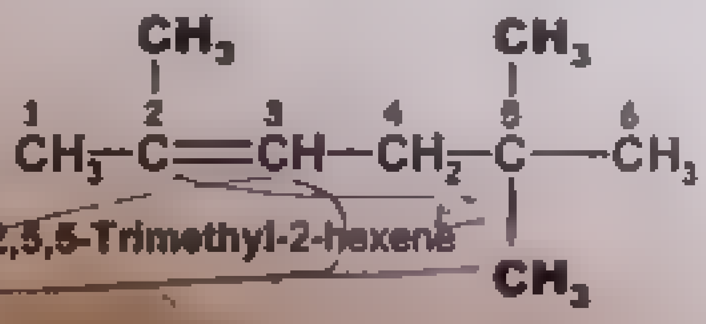


2-ene [illegible]

(5) The lower number of C-atom is placed before the name of parent alkene
(6) Alkyl groups are indicated by the methods mentioned in alkane

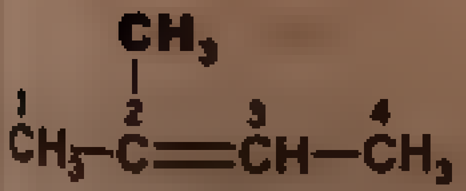


2-Ethyl-3-methyl-1-butene

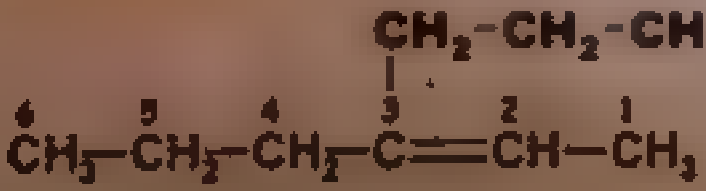


2,5,5-Trimethyl-2-hexene

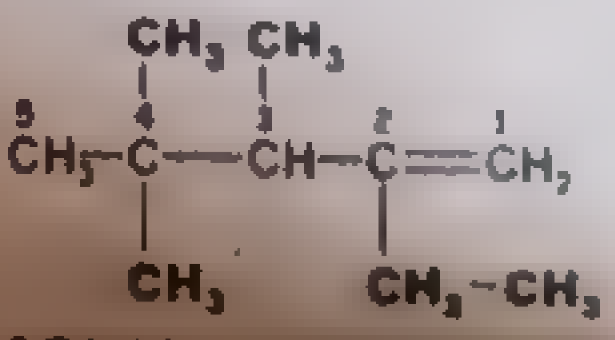
5-Methyl-2-hexene



2-Methyl-2-butene



3-Propyl-2-hexene



2-Ethyl-3,4,4-Trimethyl-1-hexene

(2) ... or 1,3-Butadiene

$H_2C=CH-CH=CH_2$ — ... or 1,3-Butadiene

$H_2C=CH-C(CH_3)=CH_2$ — 2-Meth ...

ACTIVITY

1. *Name the following Olefins by the IUPAC Systems*

(a) $H_2C=CH_2$ — Ethene

(b) $\overset{3}{C}H_3-\overset{2}{C}H=\overset{1}{C}H_2$ — 1-Propene

(c) $\overset{5}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H_2-CH_3$ — Hex...

(d) $\overset{1}{C}H_3-\overset{2}{C}(CH_3)=\overset{1}{C}H_2$ — 2-Methyl-1-propene

(e) $\overset{1}{H_2C}=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$ — 1,3-Pentadiene

(f) $H_2C=C=C=CH-CH-CH_3$

(g) $\overset{4}{C}H_3-\overset{3}{C}(CH_3)=\overset{2}{C}(CH_3)-\overset{1}{C}H_3$ — 2,3-Dimethyl-2-butene

(h) $\overset{6}{C}H_3-\overset{5}{C}(CH_3)_2-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_3$

2. *Name the compounds (a) and (b) by IUPAC nomenclature and compounds (c) and (d) by their trivial common names and (e) by its derived name*

(a) $\overset{1}{H_2C}=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H(CH_3)-\overset{5}{C}H_3$ — 4-Methyl-1,2-pentadiene

(b) $H_2C=C-CH-CH$ (C_2H_5)

(c) $CH_3-CH_2-CH=CH-CH_2-CH_2-CH_3$ — ...-Heptene (3-Heptene)

(d) CH ... CH ... CH

3. *Write structural formulas for the following compounds and discuss ...*

(a) 1,3-Butadiene

$H_2C=CH-CH=CH_2$

(b) 1,2-Pentadiene

$H_2C=C=CH-CH_2-CH_3$

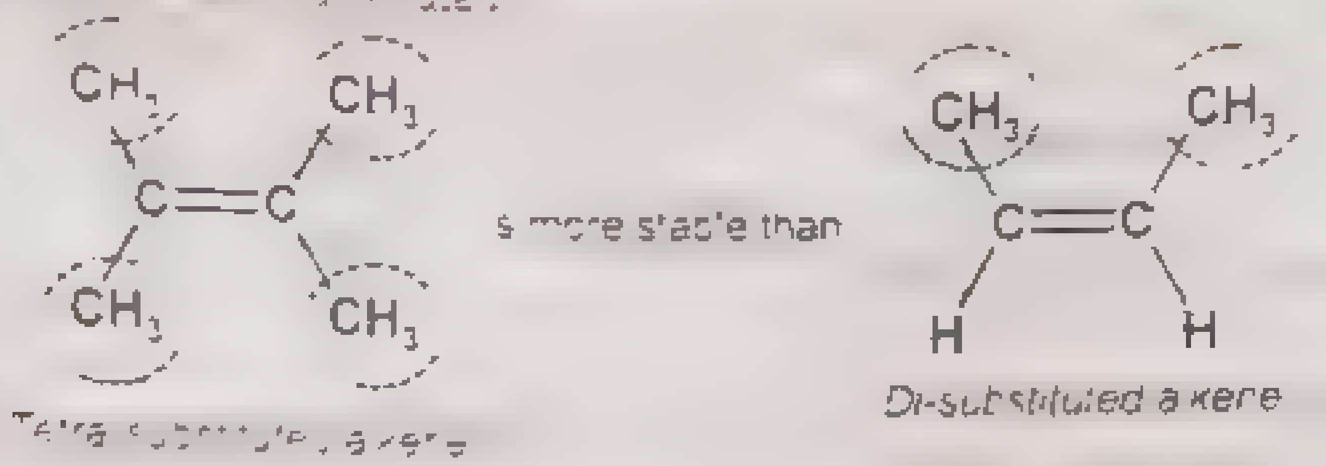
(d) 2-Methyl-1,3-butadiene

$H_2C=C(CH_3)-CH=CH_2$

H C ... CH = C ... CH

RELATIVE STABILITY

(1) Degree ... alkenes are more stable

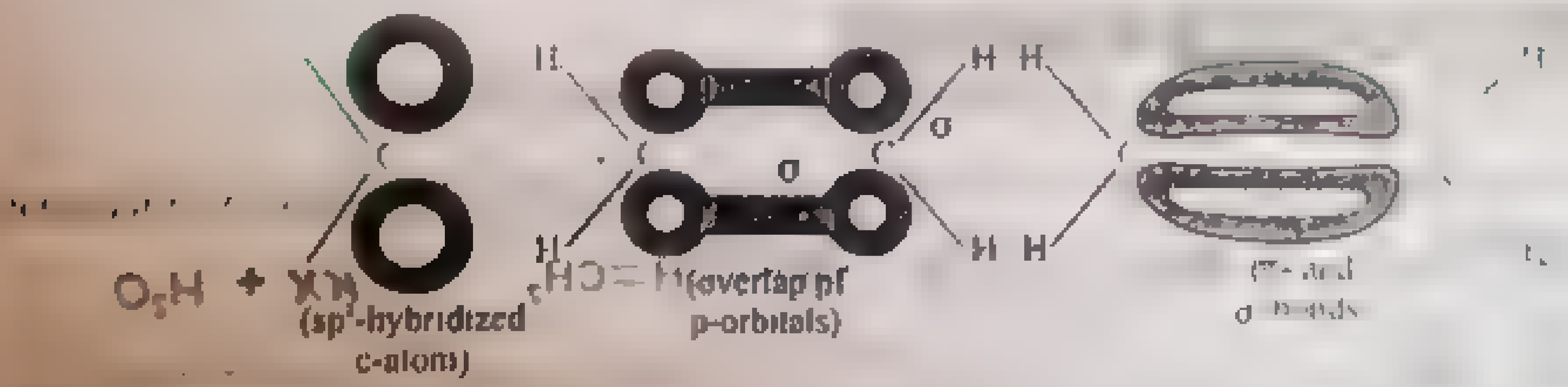


(2) Stereochemistry: trans alkenes are more stable than cis due to less steric interactions when 2 groups ... double bond e.g. trans-2-butene > cis-2-butene

(3) Conjugated alkenes are more stable than isolated alkenes
1,3-Pentadiene is more stable than 1,4-pentadiene

STRUCTURE

- The carbon atoms joined together by π bond are sp^2 hybridized
- Thus, each carbon atom has three sp^2 hybrid orbitals and one p orbital
- The hybrid orbitals form σ-bonds due to linear overlap
- The p-orbitals form π-bond due to sideways overlap



- The carbon-carbon distance in ethene is shorter (1.34Å) than the C–C ... due to increased electron density between carbon atoms

- Carbon atoms are coplanar, and the rotation of one c-atom with respect to other is restricted which results in cis-trans isomerism in alkene

PREPARATION OF ALKENES

(1) DEHYDRATION OF ALCOHOLS

H OH

H OH

H OH

$$R-\underset{OH}{\overset{CH_3}{C}}-\underset{H}{CH_2} \xrightarrow[85°C]{20\%\ H_2SO_4} R-\overset{CH_3}{C}=CH_2 + H_2O$$

Tertiary alcohol

(2) DEHYDROHALOGENATION OF ALKYL HALIDES

Removal of hydrogen halide (HX) from alky halides is called Dehydrohalogenation

Example

Alkyl halides on heating with alcoholic potassium hydroxide

$$R-\underset{H}{CH}-\underset{X}{CH_2} + KOH \xrightarrow{alcohol} R-CH=CH_2 + KX + H_2O$$

$$\underset{H}{CH_2}-\underset{Br}{CH_2} + KOH \xrightarrow{alcohol} H_2C=CH_2 + KBr + H_2O$$

Bromoethane

$$CH_3-\underset{H}{CH}-\underset{Br}{CH_2} + KOH \xrightarrow{alcohol} H_3C-CH=CH_2 + KBr + H_2O$$

1 Bromopropane

ACTIVITY and REACTIONS

HYDROGENATION

The process in which a molecule of hydrogen is added to an alkene in the presence ... moderate pressure (1-5atm) to give a saturated compound is known as catalytic hydrogenation.

Examples and Explanation

- ... Heat of Hydrogenation
- ...
- The catalysts employed are Pt, Pd and Raney ...

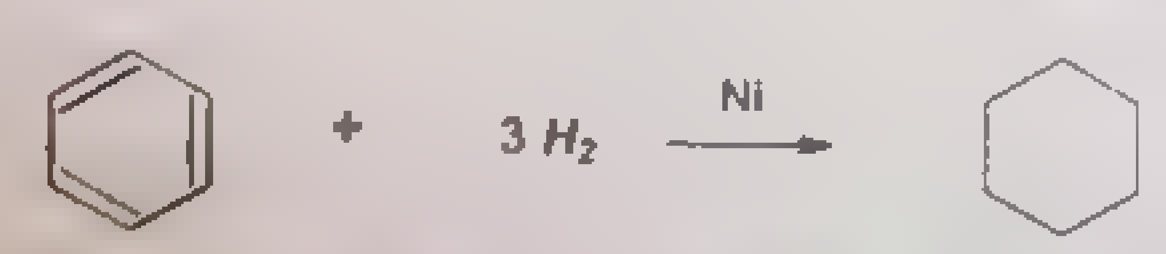
Raney Nickel

It is prepared by treating ...

$$Ni - Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + \frac{3}{2} ...$$

Examples.

3-Methyl-1-butene



Benzene — Cyclohexane

Catalytic hydrogenation has many applications
- In industry, vegetable ghee is prepared by catalytic hydrogenation of vegetable oil
- The reaction is quantitative, therefore, it is used in laboratory for analytical purpose
- It is also used as synthetic method in laboratory

HYDROHALOGENATION

The electrophilic addition ... hydrohalic acids ... compound ... hydrogen

Alkenes react with aqueous solution of halogen acid to form alkyl halides

Ethylene — Chloroethane

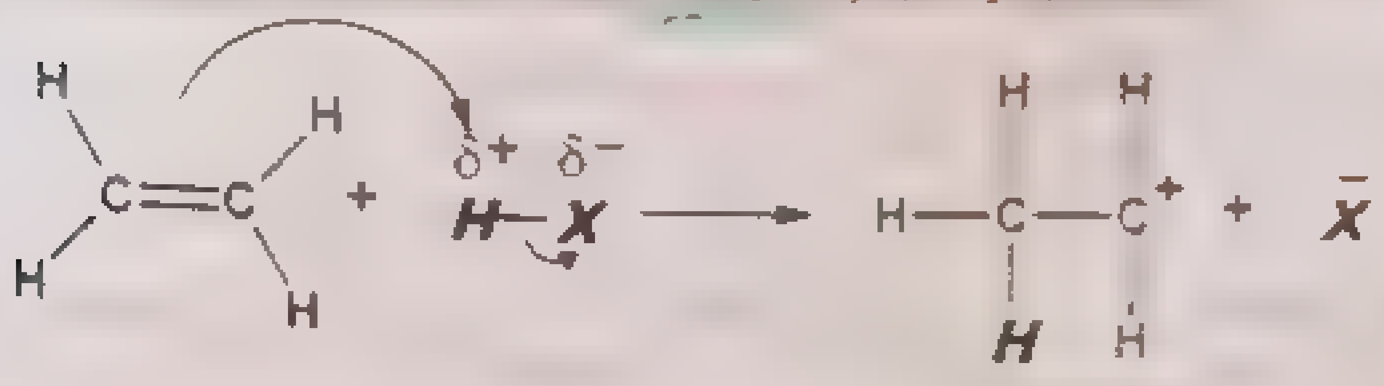
The order of reactivity of halogen acids is HI>HBr>HCl

Mechanism

The process occurs in two steps

Step – 1

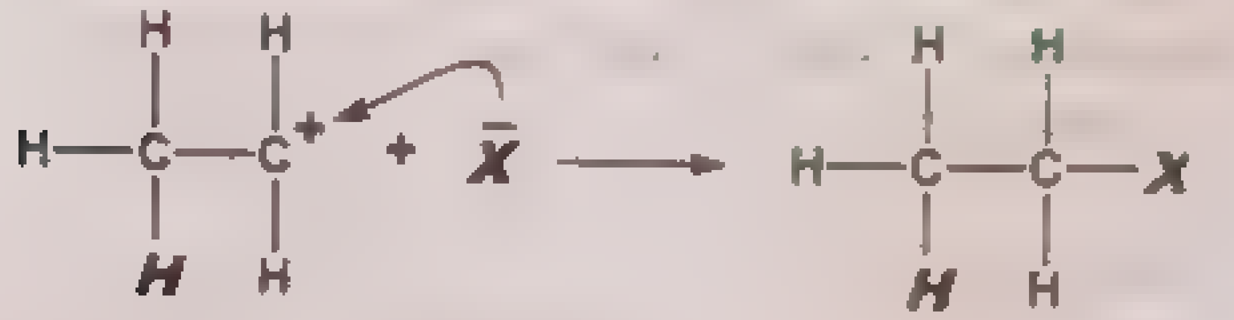
In first step proton of HX adds to [illegible]



Carbocation

Step – 2

In second step, halide ion combines with carbocation to give alkyl halide



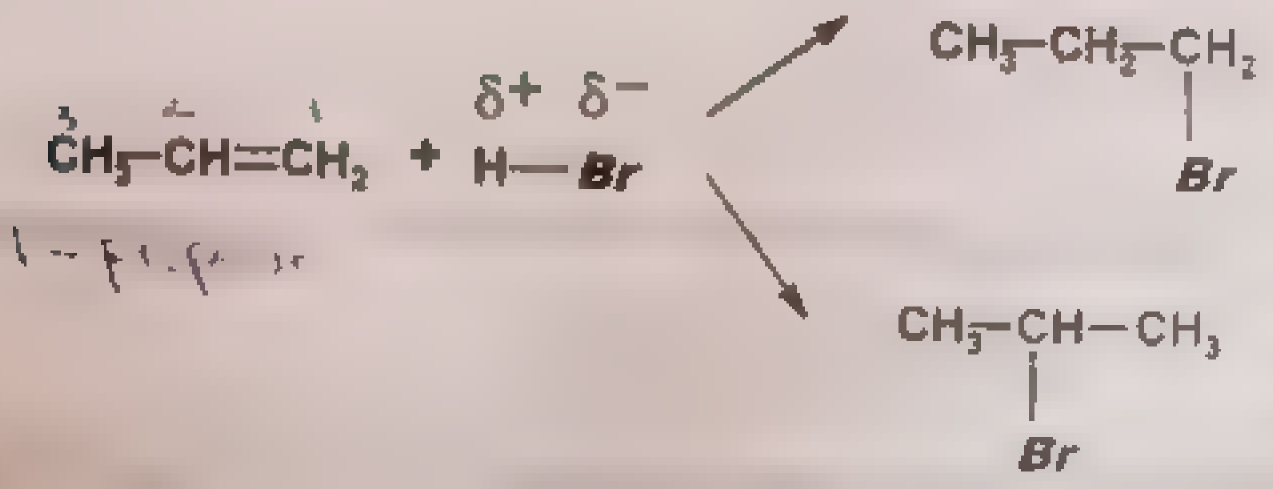
Markownikov's Rule

The addition of HX to unsymmetrical alkenes follows Markownikov's Rule.

It states

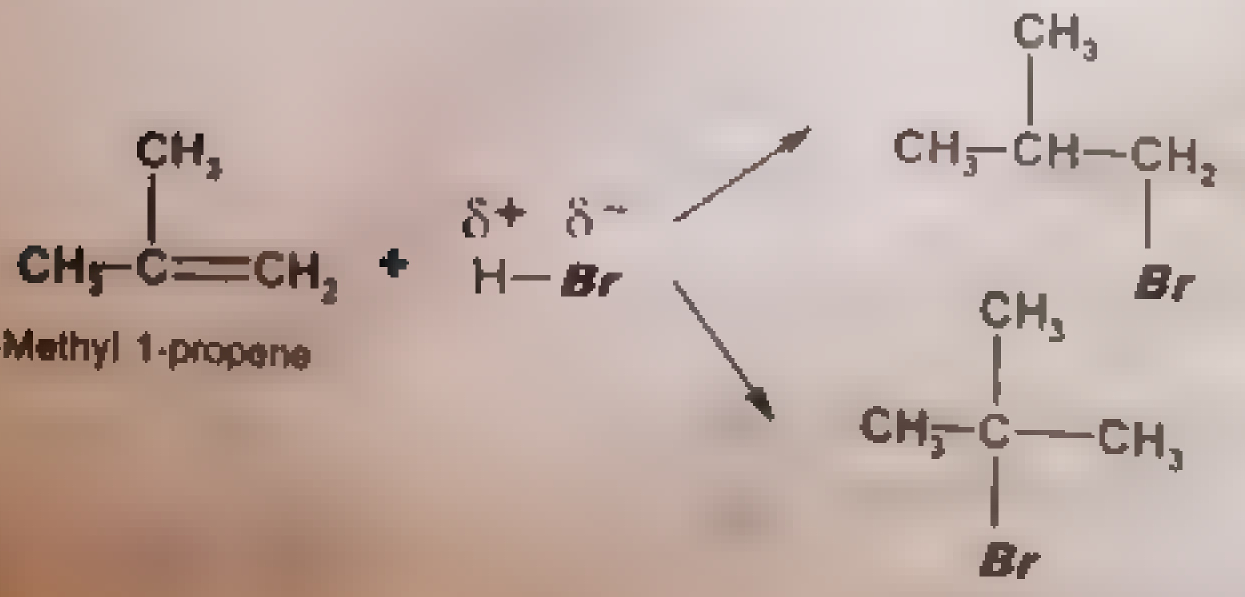
In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms

Examples:



1-Bromopropane (not formed)

2-Bromopropane (actual product)



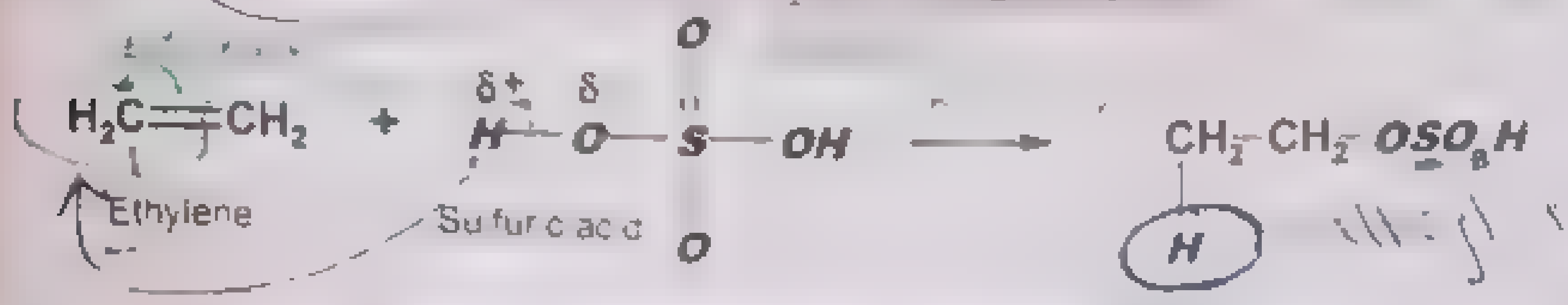
2-Methyl 1-propene

1-Bromo-2-methyl propane (not formed)

2-Bromo-2-methyl propane (actual product)

3) HYDRATION

Some reactive alkenes react with water in the presence of suitable substances ...
It is possible as alkenes are soluble in cold conc. sulphuric acid ...
(i) Alkenes dissolve in conc. H_2SO_4 and form alkyl hydrogen sulphates

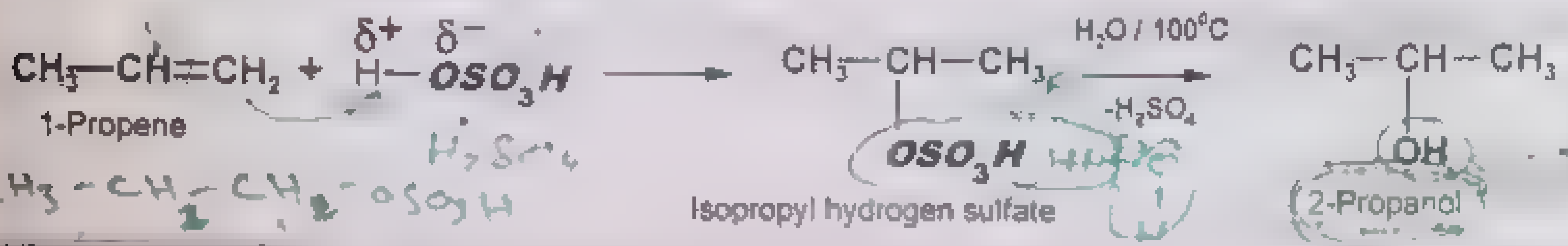


(ii) Alkyl hydrogen sulphates on boiling with water give alcohols

$$CH_3-CH_2-OSO_3H + H-OH \xrightarrow{100^\circ C} CH_3-CH_2-OH + H_2SO_4$$

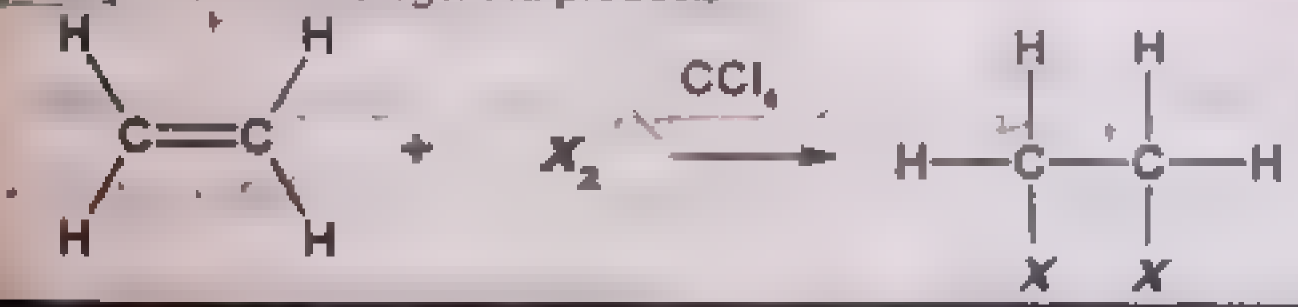
Ethanol

The reaction follows Markownikoff's rule



(4) HALOGENATION

The alkenes react with halogen in an inert solvent like carbon tetrachloride at room temperature to give ... dihalides or 1,2 dihalogenated products



a vicinal dihalide or vic-dihalide

Remember! A vicinal or vic-dihalide has two halogens on adjacent carbon atoms.

Br_2 and Cl_2 are effective electrophilic reagents. Reaction of F_2 is too fast to control. I_2 does not react.

Mechanism

The reaction occurs in two steps

Step - 1

A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.

Step - 2

The nucleophilic bromide ion then attacks on the carbon of the bromonium ions to form ... The color of bromine is discharged

In this reaction red colour of Br_2 is discharged. So this reaction is used to detect the presence of double bond in a compound.

(5) HALOHYDRATION

Addition of hypohalous acid (HOX) is called halohydration.

- Alkenes react with hypohalous acid to give halohydrin.
- In this reaction, molecules of the solvent (water) become reactant.

$$X_2 + H_2O \longrightarrow HX + HOX \qquad (X_2 = Cl_2 \text{ or } Br_2)$$

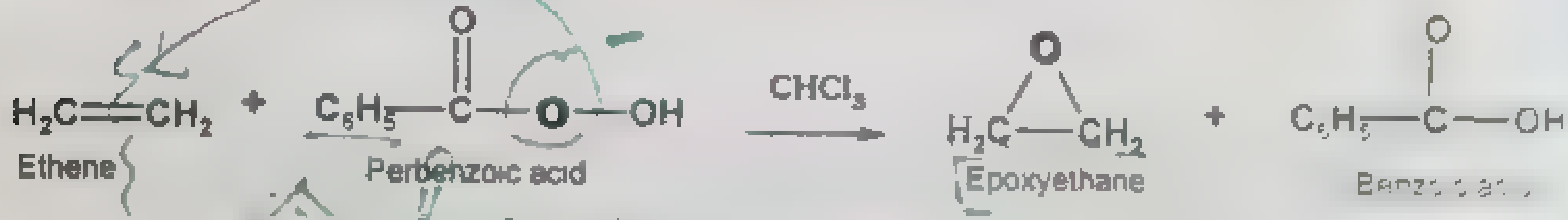
Halohydrin

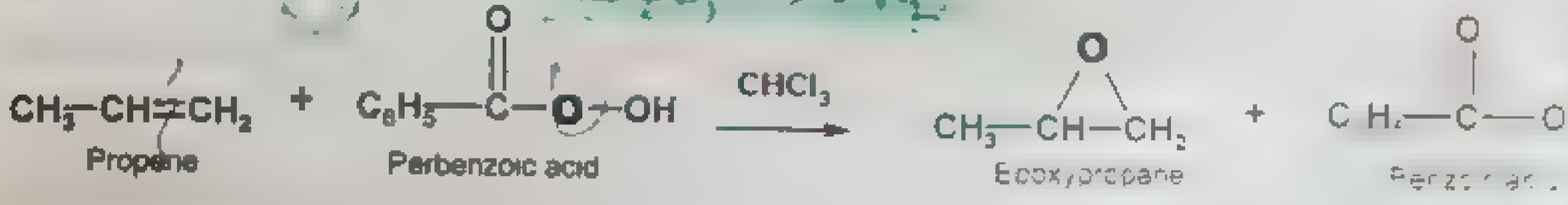
The reaction follows Markownikoff's rule

$$CH_3-CH=CH_2 + \overset{\delta-}{HO}\overset{\delta+}{X} \longrightarrow CH_3-\underset{OH}{CH}-\underset{X}{CH_2}$$

(6) EPOXIDATION

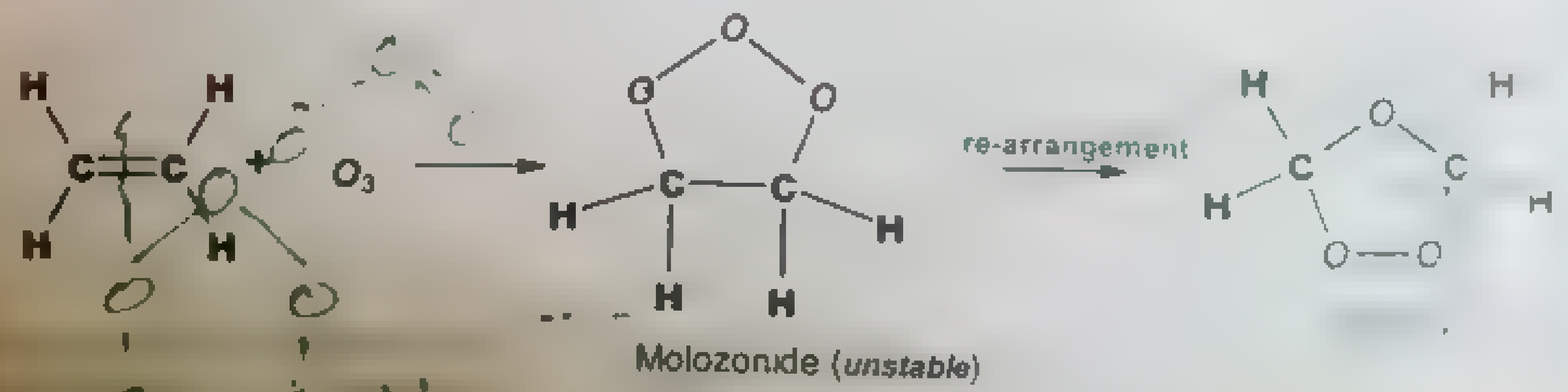
- It is the formation of epoxides.
- Peracids such as peroxyacetic acid or peroxybenzoic acids react with alkene to form epoxides.





(7) OZONOLYSIS

Ozone (O_3) reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to ozonide,



REDUCTION OZONIDE

Ozonides are unstable compounds and are reduced directly on treatment with zinc and H_2O. The reduction produces carbonyl compounds (aldehydes or ketones)

$$Zn + H_2O_2 \longrightarrow ZnO + H_2O$$

- Ozonolysis is used to locate the position of double bond in an alkene
- The C-atom of double bond is changed to carbonyl group

POLYMERIZATION

Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.

Ethene polymerizes to polythene at 400 °C at a pressure of 100 atm

$$\underset{\text{Ethylene}}{n\,H_2C{=}CH_2} \xrightarrow[\text{traces of } O_2\ (0.1\%)]{100\ \text{atm}\ /\ 400^\circ C} \underset{\text{Polyethylene}}{\left[\!-CH_2-CH_2-\!\right]_n}$$

Good quality of polyethylene is also produced by polymerization of ethene in the presence of a [illegible] $Al(C_2H_5)_3]$ and titanium tetrachloride ($TiCl_4$) catalysts.

Interesting Information

Examples of natural and synthetic polymers

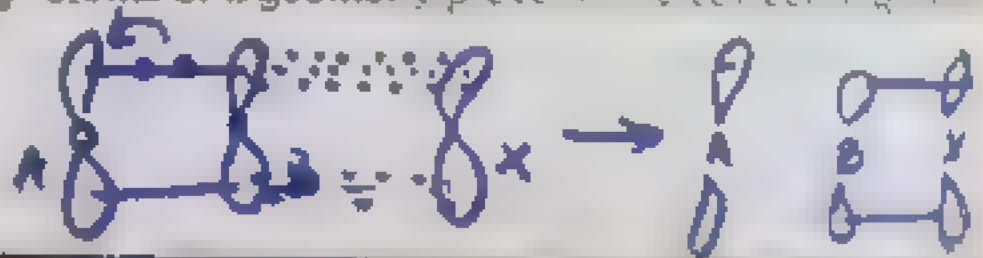
	Polyhmer	Monomer	Where your find it
Natural	Protein	Amino acids	Wool, silk, muscle, etc
	Starch	Glucose	Potato, wheat, etc
	Cellulose	Glucose	Paper, wood, dietary fibre chromosomes
	DNA	Nucleotides	genes
Synthetic	Poly (ethane)	Ethene	Bags, washing-up bowls, etc
	Poly (chloroethene) (PVC)	Chloroethene	Fabric coatings, electrical insulation, toys
	Poly (phenylethene) (polystyrene)	Phenylethene	expanded polystyrene
	polyester	Ethane-, 2-diol and benzene- 1, 2-dicarboxylic acid	Skirts, shirts, trousers

CONJUGATION

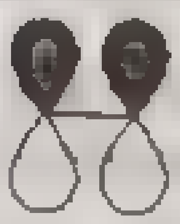
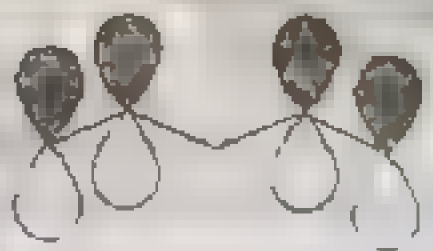
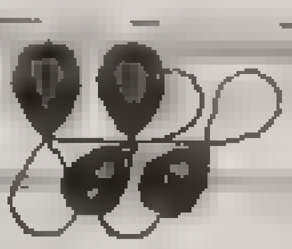
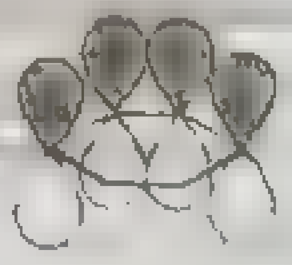
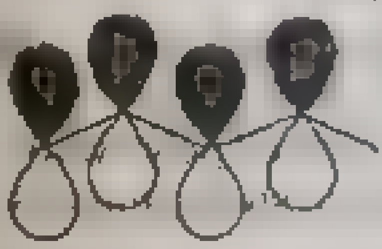
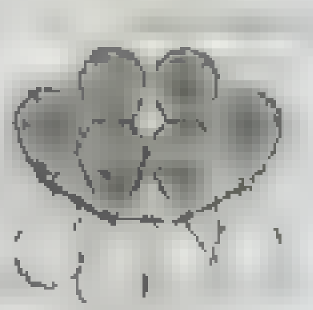
- The word **conjugation** is derived from a Latin word that means "*to link together*"
- In organic chemistry, it is used to describe the situation that occurs when p- systems are "linked together"
- An "**isolated**" p- system exists only between a single pair of adjacent atoms (e.g. C=C
- An "**extended**" p- system exists over a longer series of atoms (e.g. C=C-C=C or C=C-C=O e
- An extended p –system results is an extension of the chemical reactivity

Fundamental Condition of a Conjugated System

- A conjugated system requires that there is a continuous array of "p" orbitals that can align to produce a bonding overlap along the whole system
- If a position in the chain does not provide a "p" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point



Examples:

System	p system	Type	System	p system	Type
Ethene		isolated	1,4-Pentadiene		isolated
Propene		isolated	1,3-Cyclopentadiene		...gated
1,2-Propadiene (Allene)		cumulated	1,3-Cyclohexadiene		[illegible]
1,3-Butadiene		conjugated	1,4-Cyclohexadiene		[illegible]
1,3-Pentadiene		conjugated	Benzene		...ed

The result of conjugation is that there are extra p bonding interactions between the ... an overall stabilization of the system

QUICK QUIZ 3

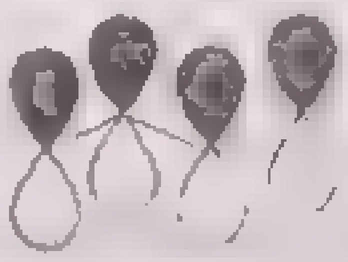
What is Conjugation?

The word "**conjugation**" is derived from a Latin word that ...
In organic chemistry, it is used ...
an "**extended**" p system exists over a longer series ...

Example:

$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

1,3-Butadiene



What are conjugated alkenes?

The alkenes in which an "extended ...

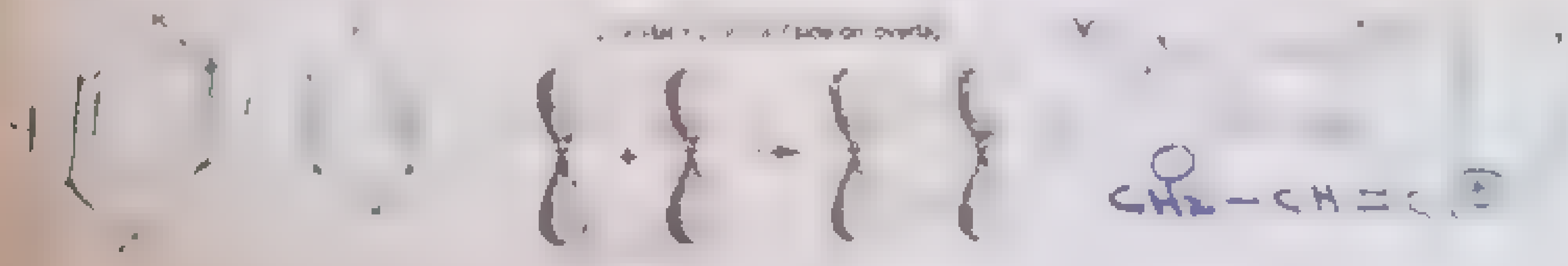
Example

$H_2C=CH-CH=CH_2$ $\qquad$ $H_2C=CH-CH=CH-CH=CH_2$

1 3-Butadiene

What is pi bond

A bond formed between ... p-atomic orbitals whose ...



π bond formation

What are s and p orbitals

When the value of azimuthal quantum number is 0 ... It can have maximum two electrons.

When the value of azimuthal quantum ... three orbitals p_x, p_y and p_z. These orbitals are ... orbitals can have maximum two electrons each. ...

What is dehydration

Removal of water molecule is called dehydration.

Example

When vapours of alcohol are passed over heated ... alkene

$$\underset{\text{Alcohol}}{R-\underset{H}{CH}-\underset{OH}{CH_2}} \xrightarrow[340-400°C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

6. What is dehydrohalogenation

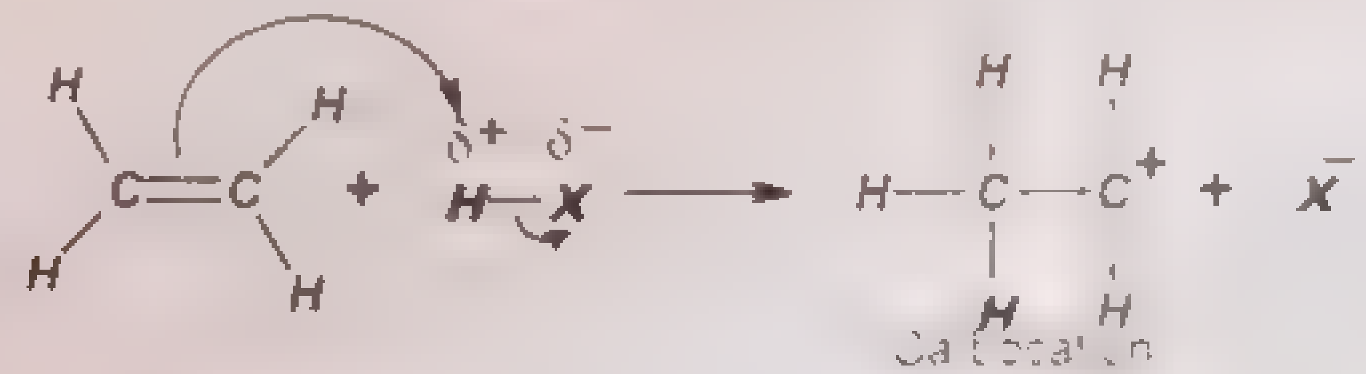
... from alky halides is called Dehydrohalogenation.

Example

7. What is hydrogenation

8. What is carbocation

A carbocation is a reaction intermediate. It is trivalent with a positive charge on carbon atom. It can produced as follows

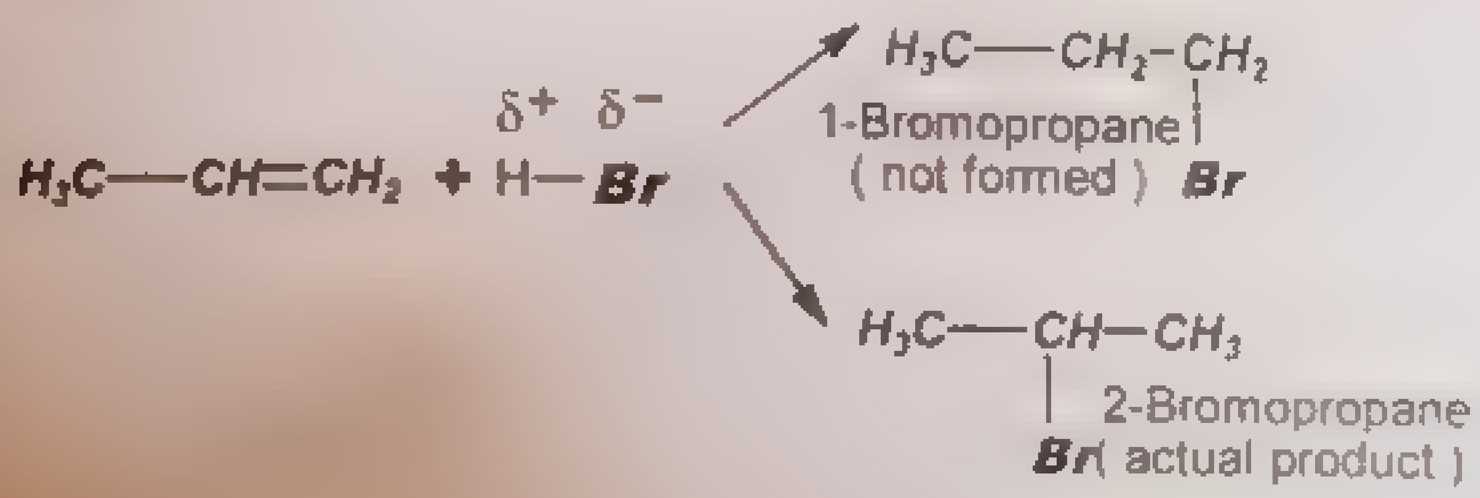


9. What is Markownikov's rule?

It states

In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond which has least number of hydrogen atoms.

Example:



10. What is electrophilic reagent?

An electron deficient reagent ... e.g.

11. What is nucleophilic reagent?

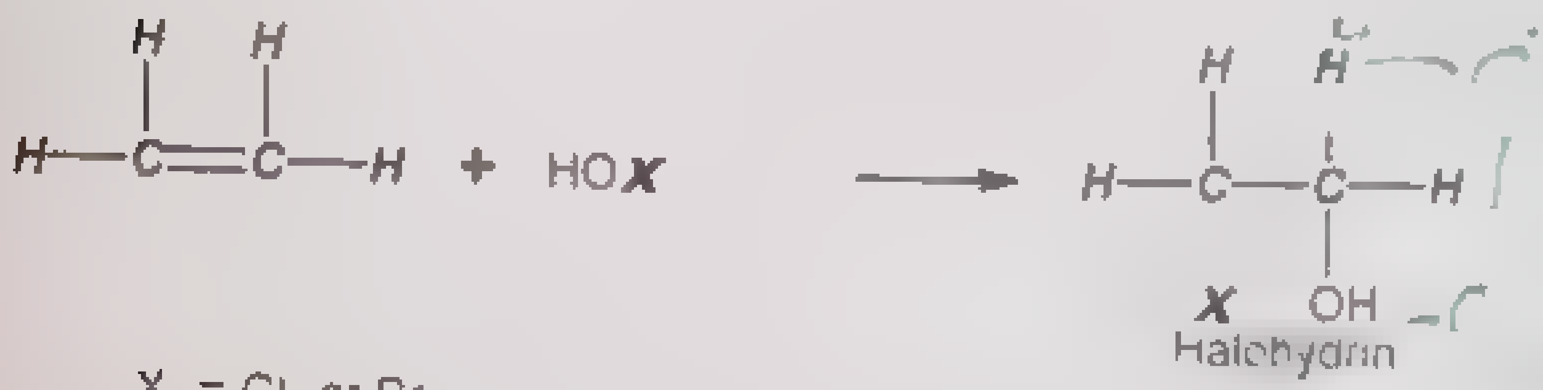
An electron rich reagent ... e.g.

12. What is halohydration?

Addition of hypohalous acid HOX ...

Alkenes react with hypohalous acid to give Halohydrin. In this reaction, molecules of the ... reactants too.

$$X_2 + H_2O \longrightarrow HX + HOX$$



$X_2 = Cl_2$ or Br_2

13. What is polymerization

- Polymerization is a process in which a small organic molecules which ... together to form larger molecules. The substances so produced are called polymers
- Ethene polymerizes to polythene at 400 °C at a pressure of 100 atm

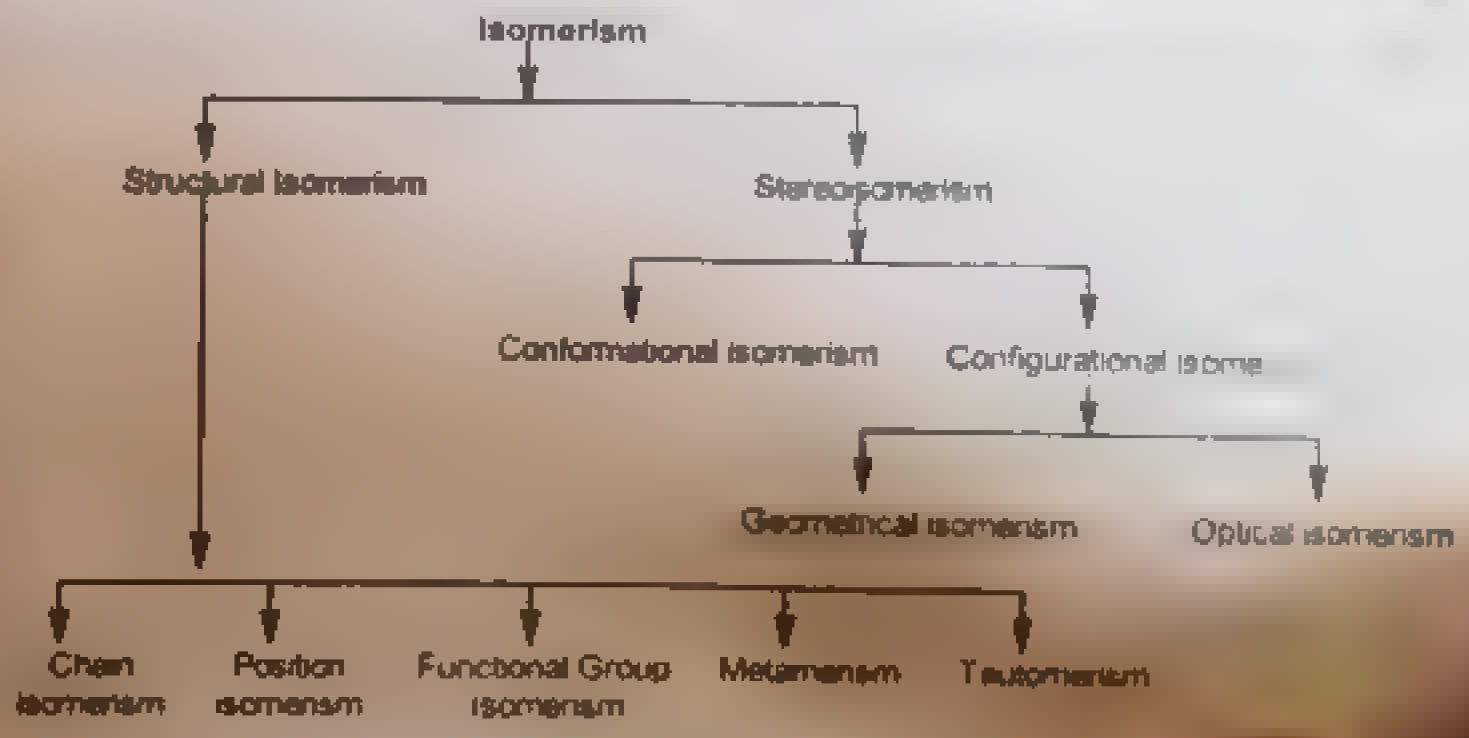
$$n\,H_2C{=}CH_2 \xrightarrow[\text{traces of } O_2\ (0.1\%)]{100\ \text{atm}\ /\ 400^{\circ}C} -\!\!\left[CH_2-CH_2\right]\!\!-_n$$

Ethylene — Polyetheylene

Exercise Q3(1). What is isomerism? Explain different types of isomerism?

ISOMERISM

Compounds that have the same molecular formula but different chemical structures are called isomers and the phenomenon is called isomerism.



The difference in properties of isomers must be due to different modes of combination or arrangement of atoms within the molecule.

Configuration:

The term configuration is the three-dimensional arrangement of atoms that characterizes a particular compound.

There are t...

(1) ...al Isomerism

(2) Stereoisomerism

STRUCTURAL ISOMERISM

When the isomerism is due to difference in the arrangement of atoms within the molecule without any reference to space, the phenomenon is called Structural Isomerism

Structural Isomers are compounds that have the same molecular formula but different structural formu...

Structural isomerism is of five types

(a) Chain isomerism

(b) Position isomerism

(c) Functional isomerism

(d) Metamerism

(e) Tautomerism

STEREOISOMERISM

When isomerism is caused by the different arrangements of atoms or groups in space the phenomenon is called Stereoisomerism.

- The stereoisomers have the same structural formulas but differ in arrangement of atoms in s...
- Stereoisomer is exhibited by such compounds which have the same structural formula b... configuration

Two important types of stereoisomerism are

(a) Geometrical or *cis-trans* Isomerism

(b) Optical Isomerism

CHIRAL CENTER

The center in a molecules due which molecule becomes asymmetric is called a ...

PLANE OF SYMMETRY

A plane which divides an object into two symmetrical halves, is said to be plane of symmetry.

Examples and Explanation:

- A person or a hat has a plane of symmetry
- A person's hand or gloves lack plane of symmetry
- An object lacking a plane of symmetry is called dissymmetric or Chiral (pronounced as Ki-ral).
- A symmetric object is referred to as Achiral
- A dissymmetric object cannot be superimposed on its mirror image

Planes of Sym...

e.g. A left hand does not ... another left hand ... on each other. If ... the thumb would clash.

The mirror image relationship ...

It should be noted that right ...

Chiral molecule has at least one asym...

Chiral objects

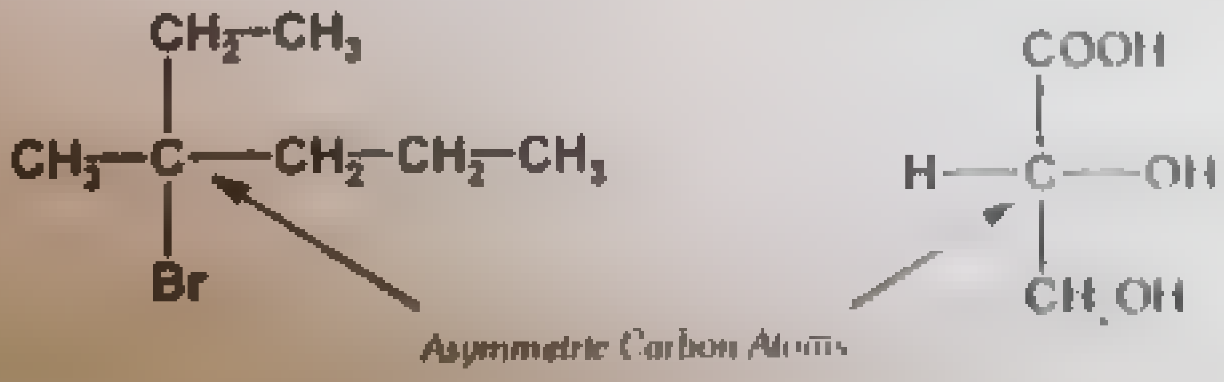
- An achiral molecule has a plane of symmetry.

Achiral objects

CARBON-BASED CHIRAL CENTERS:

A carbon atom which is bonded to four different groups is called an Asymmetric Carbon Atom or Chiral Carbon Atom.

Examples:



- The term asymmetric carbon atom is misleading. It only means that a carbon atom ... groups. Such type of molecule lacks plane of symmetry and is called asymmetric ... without symmetry.
- Presently the term Dissymmetric or Chiral Molecules is often used for asymmetric molecules.

OPTICAL ACTIVITY

A substance that can rotate plane of polarized light is called optically active and this property of a substance is called optical activity

Explanation

- Electromagnet ... in all possible planes. When this light is passed through a Nicol prism (made of calcite CaCO$_3$) ... allows only those radiation to pass through it, which are parallel to its axis. This light ... is called plane polarized light or simply polarized.
- When plane polarized light will pass through a solution of an optically active compound, the compound will rotate the plane polarized light either to left or right. These compounds are said to be Optically Active. This property of a compound is called Optical Activity.
- Dextrorotatory Compound

  The compound which rotates the plane of polarized light towards right (clock-wise), is called a dextrorotatory compound. It is indicated by the sign (+) sign

- Leavororotatory Compound

  The compound which rotates the plane of polarized light towards left (anticlock-wise), is called a leavorotatory compound. It is indicated by the sign (–) sign

Measurement of Optical Rotation

The instrument ... measure direction and magnitude of optical rotation is called Polarimeter

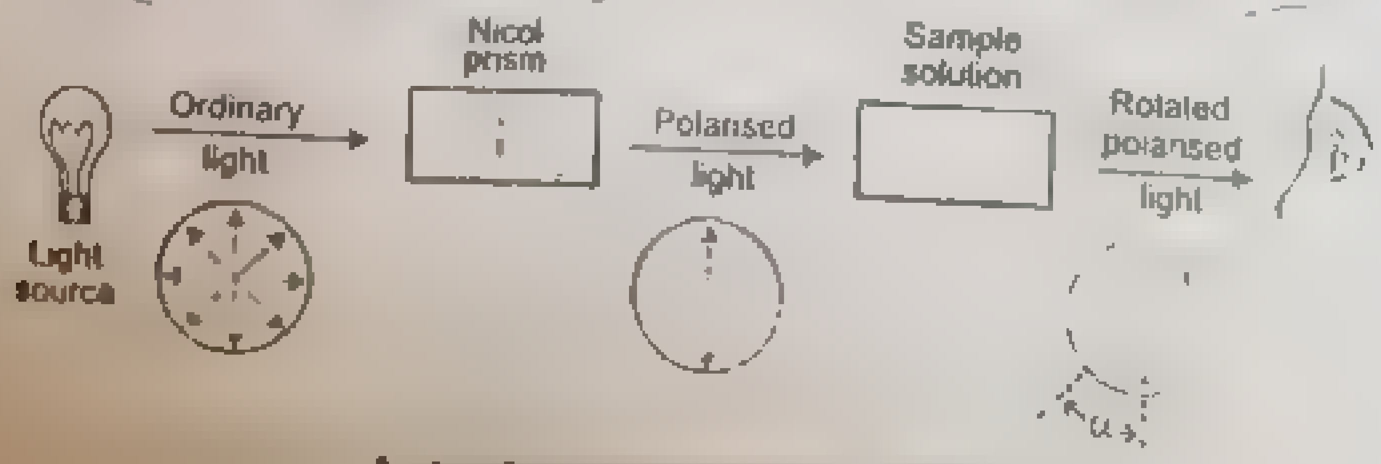
Construction

It has following basic parts

- Fixed polarizer (Nicol prism) to polarize light
- Movable analyzer (Nicol prism)
- A tube containing (sample solution) placed between polarizer and analyzer
- A light source

Working

- Light from light source passes through polarizer and is polarized. If the sample tube is empty ... parallel position of polarizer and analyzer gives maximum illumination. This is the zero reading.
- Now a solution of known concentration of an optically active compound is ... the sample tube. The solution will rotate the plane polarized light through a certain number of degrees. ... through analyzer and there will be less illumination.
- In order to get maximum illumination again, analyzer is rotated, the angle through which analyzer is rotated gives the magnitude of observed rotation (α).
  - ✓ *If rotation is to the right, it is said to be (+) and the compound is called dextrorotatory*
  - ✓ *If rotation is to the left, it is said to be (–) and the compound is called leavotrorotatory*



A simple polarimeter in operation

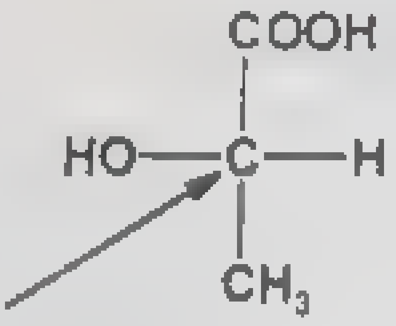
STEREOISOMERISM: OPTICAL ISOMERISM

An optically active compound can exist in two isomeric forms which rotate the plane polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical Isomerism

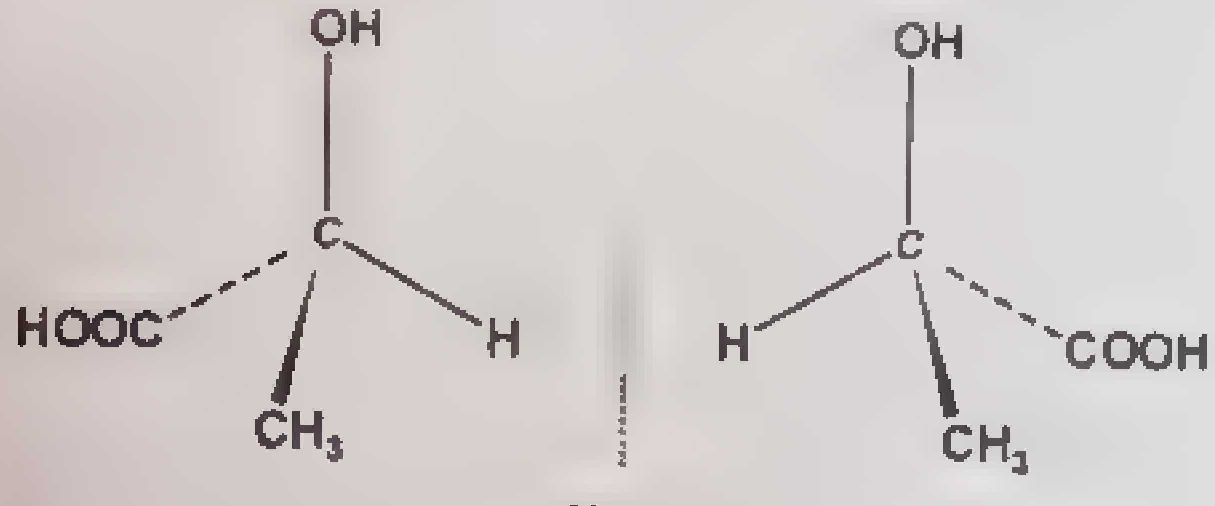
- *The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as Dextrorotatory Isomer or (+) isomer*
- *The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the Laevorotatory Isomer or (-) isomer*

Optical Isomerism of Lactic Acid

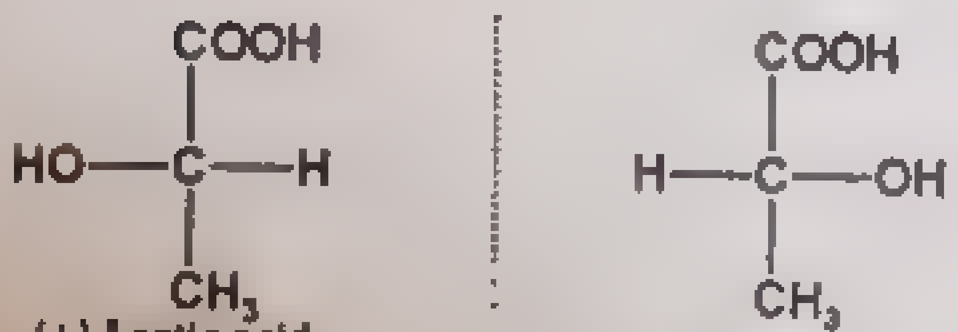
- Lactic acid (2-Hydroxypropanoic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.
- Two three dimensional structures are possible for Lactic acid



Asymmetric Carbon Atoms



Mirror



(+)-Lactic acid m.p. = 26°C (I)	(−)-Lactic acid m.p. = 26°C (II)	*Equimolar mixture of (+) and (-) forms is called racemic mixture. It is denoted as (±)* *e.g. (±)-Lactic acid* (III)

- These structures are not identical because they cannot be superimposed on each other
- The non-superimposable mirror images of each other and called *Enantiomers*
- Equimolar mixture of two enantiomers is called racemic mixture. It is optically inactive and denoted by (±)
- Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive

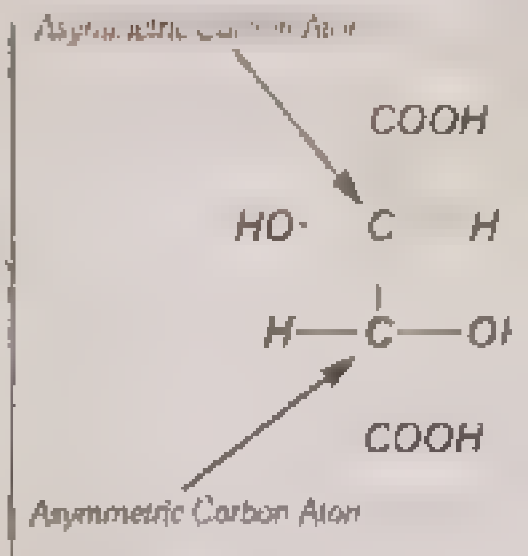
(+)-Lactic Acid: It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory

(−)-Lactic Acid: It rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (−)- Lactic acid is the mirror image of (+)-lactic acid and vice versa

(±)-Lactic Acid: It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms. It is called racemic mixture.

Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms



Two Asymmetric Carbon Atoms in Tartaric acid

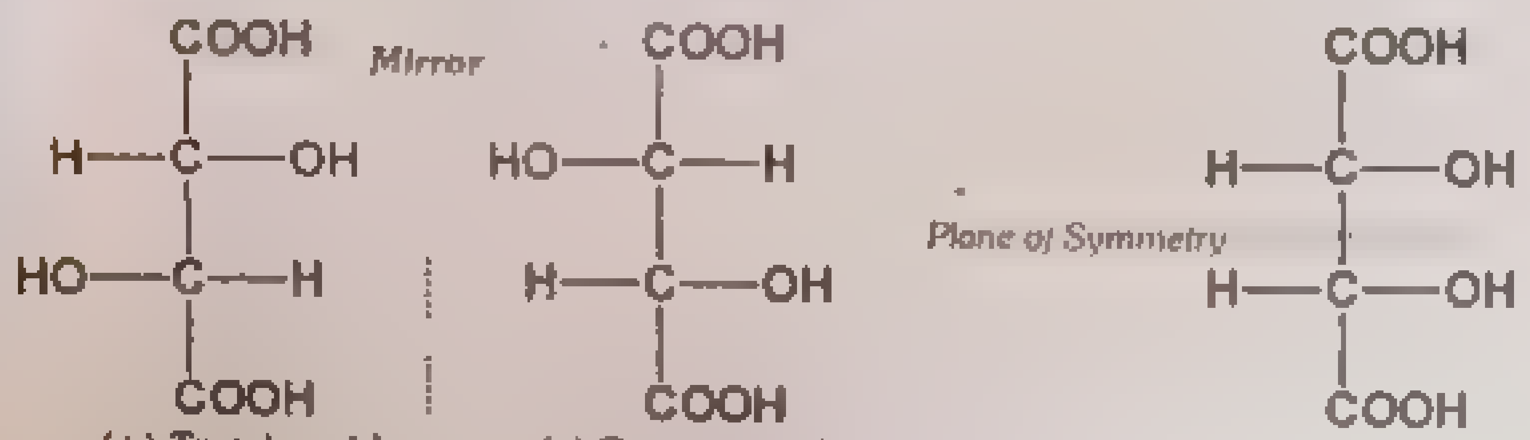
- Four forms of tartaric acid are known
- Two of them are optically active and two are optically inactive.
- The optically active forms are related to each other as a non-superimposable mirror image of each other. They are enantiomers.

(+)-Tartaric Acid It rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (–) Lactic acid is the mirror image of (+) lactic acid and vice versa

(-)-Tartaric Acid: It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

(±)-Tartaric Acid: It does not rotate the plane of polarized light. Thus it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture)

meso-Tartaric Acid It has plane of symmetry. So it does not rotate the plane of polarized light. Thus it is optically inactive



(+)-Tararic acid **m.p. = 70°C** *(Optically Active)* **(I)**

(–)-Tartaric acid **m.p. = 70°C** *(Optically Active)* **(II)**

meso-Tartaric acid *(Optically Inactive)* **(III)**

Equimolar mixture of (+) and (-) forms is called racemic mixture. It is denoted as ±

e.g. **(±)-Tartaric acid** *(Optically Inactive)* **(IV)**

Isomers of Tartaric Acid

Important!

- *In isomers of tartaric acid, (I) and (II) are enantiomers*
- *However, (I) and (III) are called diastereomers. They are not mirror image of each other*
- *Similarly, (II) and (III) are also diastereomers*

Diastereomers

Stereoisomers of the same compound which are not mirror image of each other are called diastereomers

Although enantiomers have same physical properties like melting points etc

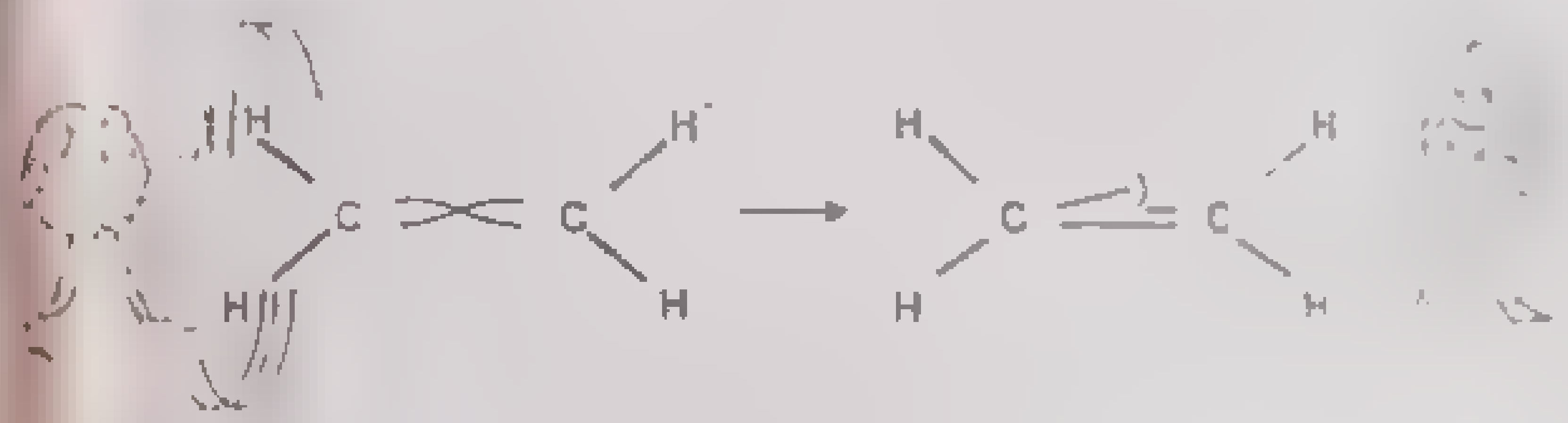
The diastereomers are totally different compounds with different physical properties

OISOMERISM & GEOMETRIC ISOMERISM

metrical isomerism (also called cis-trans isomerism) results from a restriction ... about double ... or about single bonds in cyclic compounds

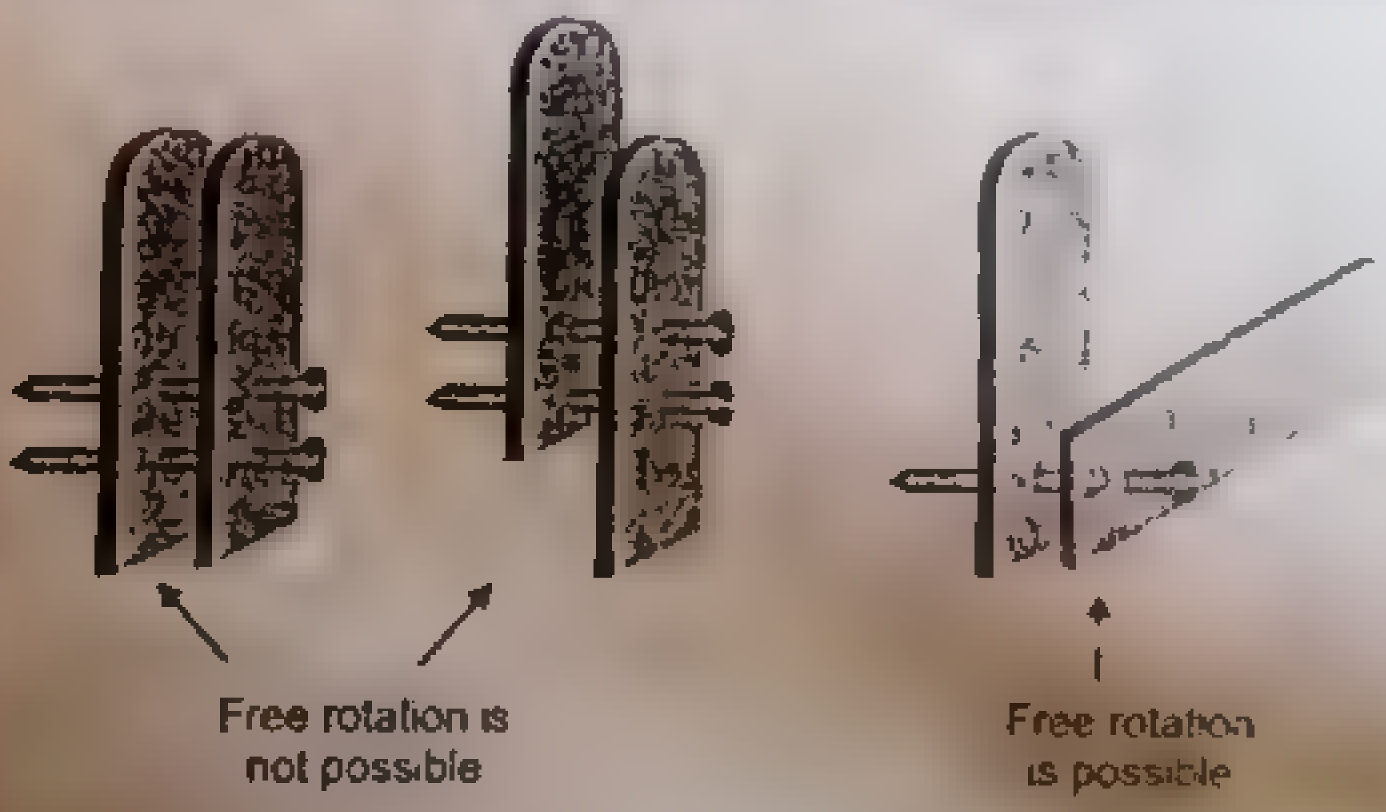
OMETRICAL ISOMERISM IN ALKENES

- The carbon atoms of the carbon-carbon d...
- The carbon-carbon double bond consists of a ...
- The sigma bond is formed by the overlap ...
- The pi bond is formed by the overlap of p orbitals
- The presence of the pi bond locks the molecule in one position
- The two carbon atoms of the C=C bond ... their position in space are fixed
- Rotation around the C=C bond is not possible because rotation would break the ...
- The restriction of rotation about the carbon-carbon double bond is responsible for the ... isomerism in alkenes



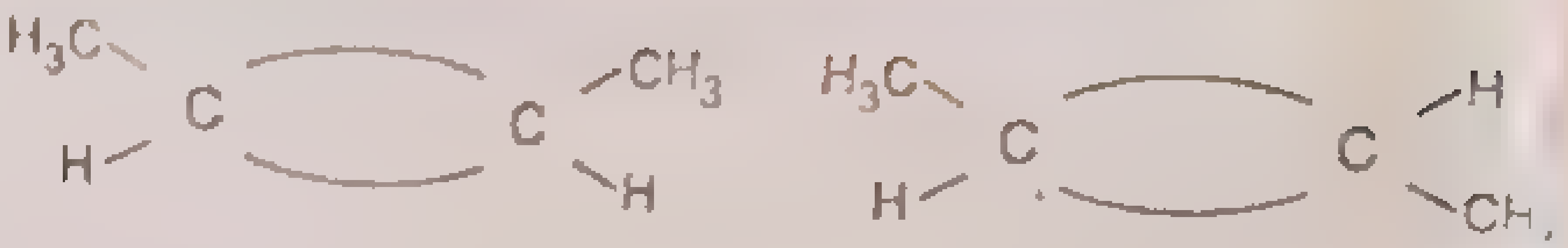
Rotation about pi bond is not possible because it would break the pi bond

A similarity for this situation is based upon two bonds and two nails ... prevent free rotation of the two bonds. But once a second nail used, the ...



Example

- Consider the case of 2 butene ...

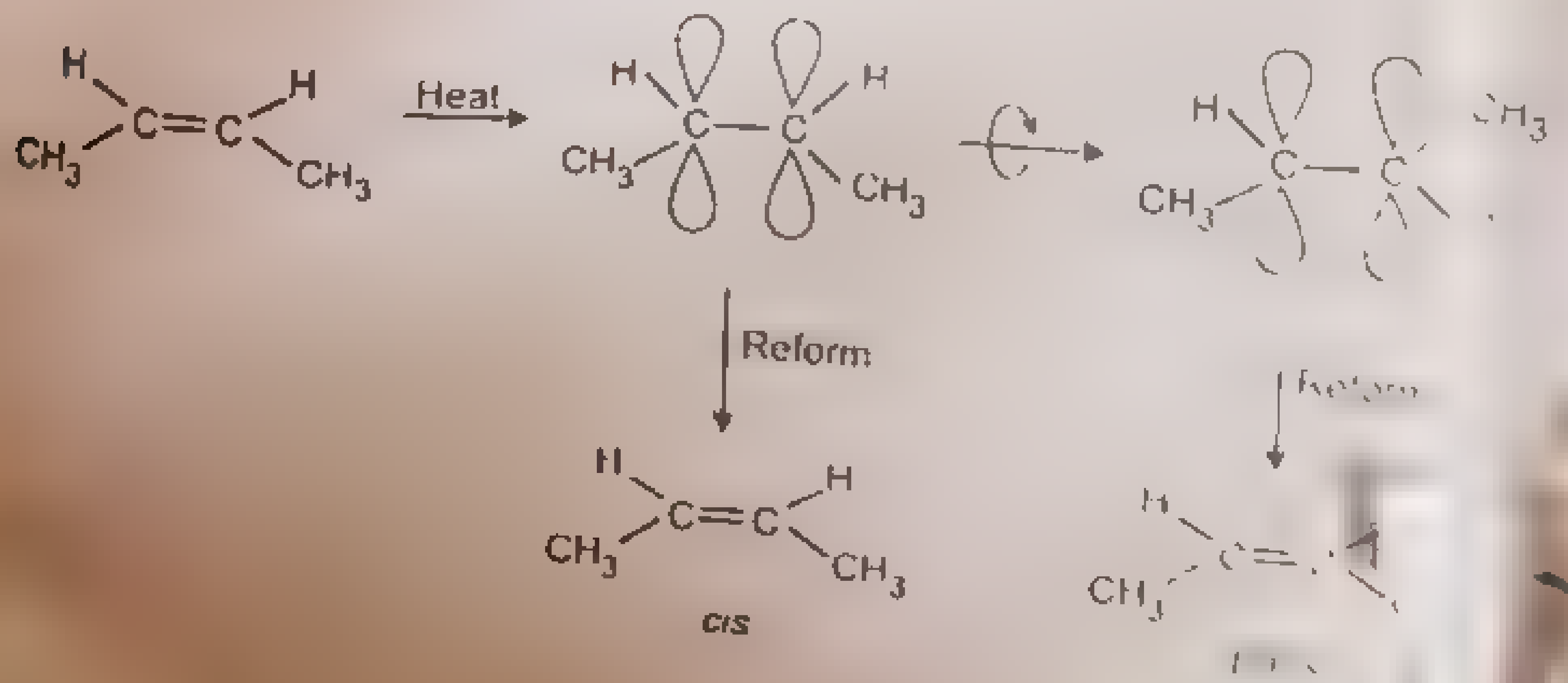


cis-2-Butene (bp 4°C) and trans-2-Butene (bp 1°C)

- These two compo nds are ca ed as geometr ca isomers. These are named as c s and tra s. Hence, this type of isomerism is also called cis-trans isomerism
  - ✓ *The cis isomer is one in which two similar groups are on the same side of the double bond*
  - ✓ *The trans isomer is that in which two similar groups are on the opposite sides of double bond.*
- Geometrical isomers are stereoisomer, because they have the same structural formula b differe arrangement of atoms.
- The geometrical isomers have d fferent physical and chemical properties
- They can be separated by conventional isomers have different physical techniques like fractional d gas chromatography etc

Inter-Conversion of cis-, trans-Isomers

- The conversion of cis-isomer into trans-isomer or vice versa ... heat high temperature or absorbs light.
- The heat supplies the energy (about 62 Kcal mole) to brea ... so that rotation about sign becomes possible
- Upon cooling, the reformation of the pi bond can take place in two ways giving mixture ... trans- plus cis-2-butene



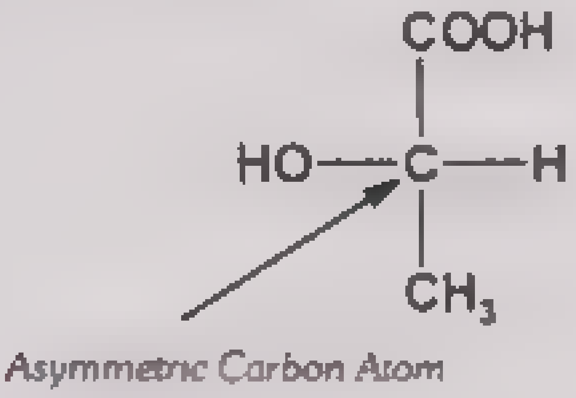
QUICK QUIZ-4

Define or explain the following terms

(a) Structural isomerism *Page 165*
(b) Stereoisomerisms *Page 156, 159*
(c) Geometrical isomerism *Page 161*
(d) Optical isomerism *Page 159*
(e) Asymmetric carbon

A carbon atom to which four different groups are attached is called an asymmetric carbon

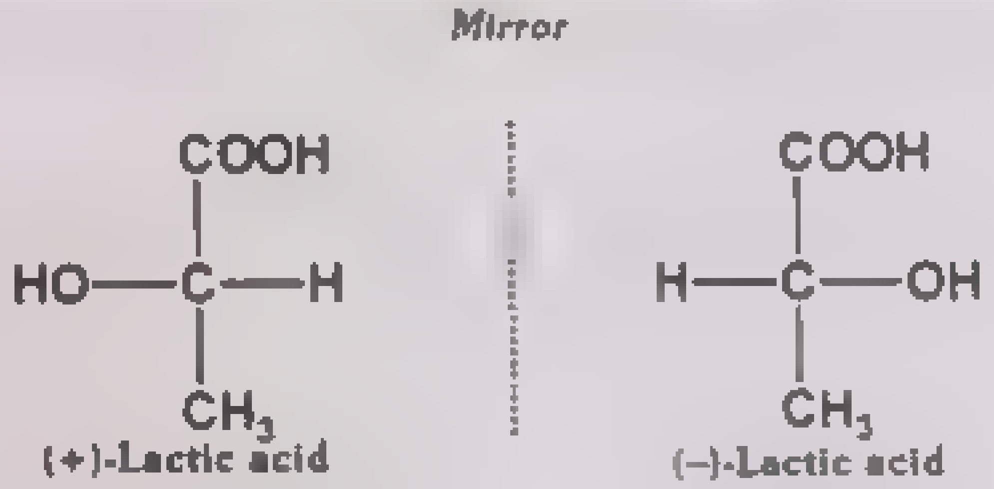
Example:



(f) Chiral molecule

A molecule which has non-superimposable mirror image is called a chiral molecule

Example: Lactic acid



(+)-Lactic acid m.p. = 26°C (I)

(–)-Lactic acid m.p. = 26°C (II)

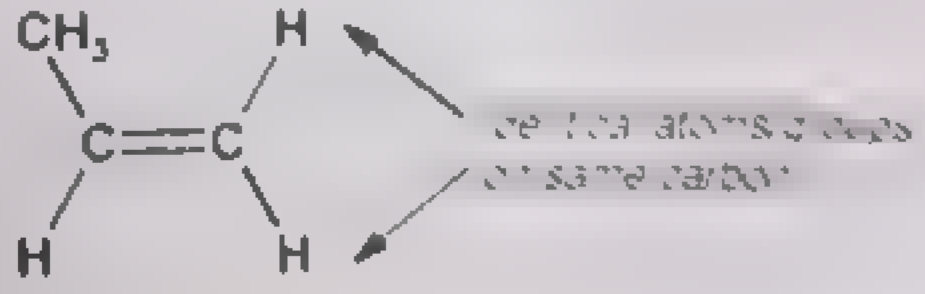
2. State the necessary condition for a compound to show geometrical isomerism. Illustrate your answer with examples

Conditions of Geometrical Isomerism

(i) Presence of double bond or cyclic ring
(ii) Two different groups must be attached, to each carbon of double bond or to different carbons of cyclic ring

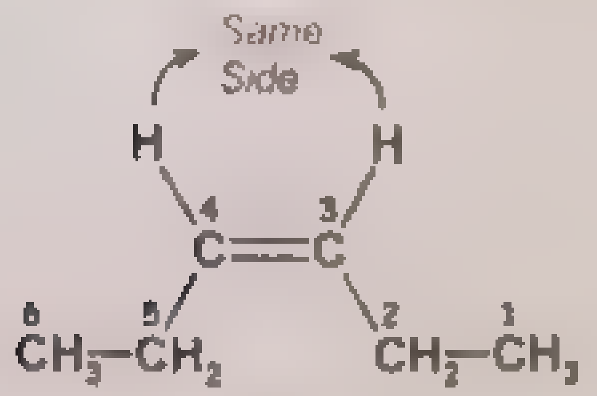
Example 1.

No geometrical isomers are possible for propene. It is because one of double bonded carbons has two identical groups (H atoms) attached to it.

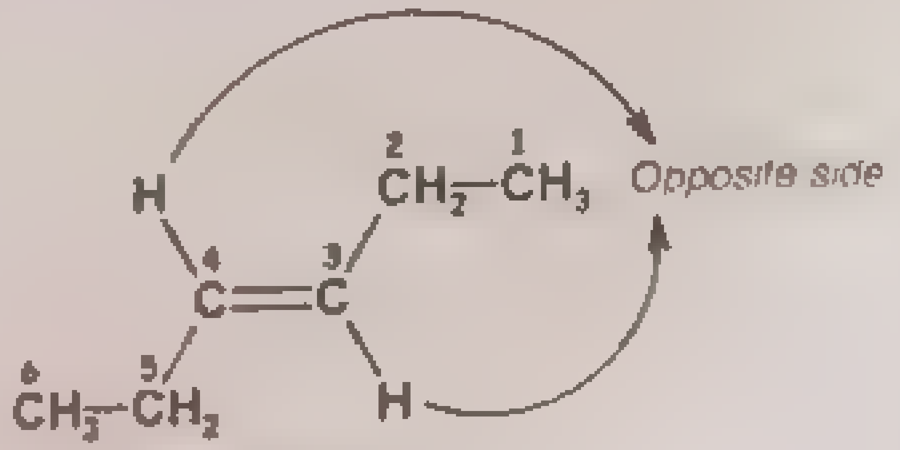


Example 2.

Geometrical isomers are possible for 3 hexene ($CH_3CH_2CH=CHCH_2CH_3$). This is because each double carbon atom is attached to two different groups (CH_3CH_2 and H)



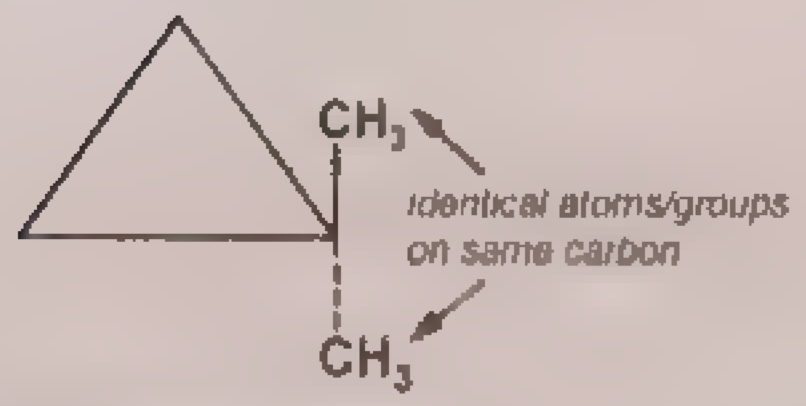
cis-2-Hexene



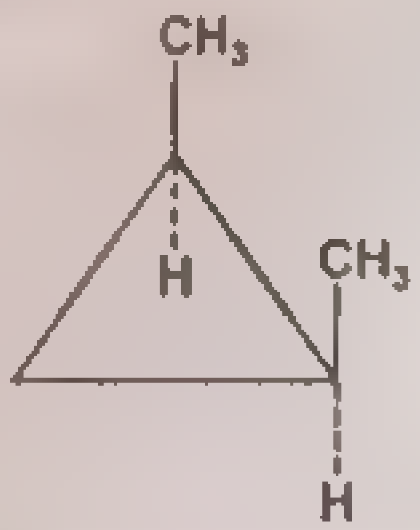
trans-2-Hexene

Example 3.

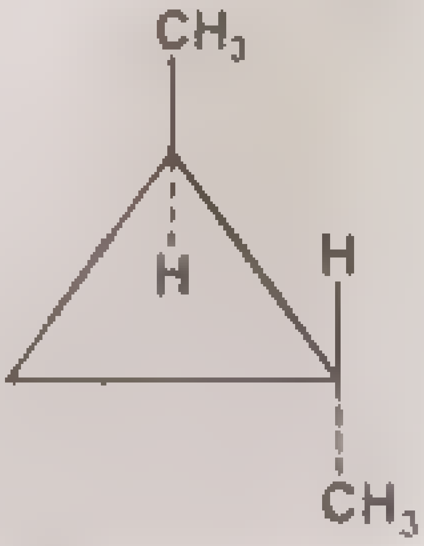
- No geometrical isomers are possible for 1,1-dimethylcyclopropane
- 1,2-dimethylcyclopropane exists in two isomeric forms



1,1-Dimethylcyclopropane



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropa

- *In cis-1,2-dimethylcyclopropane the two methyl groups are on the same side of ring*
- *In trans 1,2-dimethylcyclopropane, they are on opposite sides*

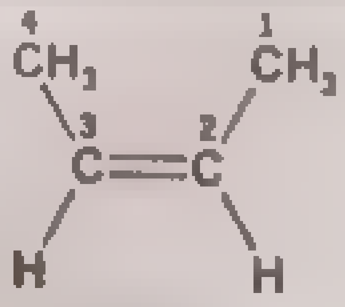
3. Which of the following compounds shows geometrical isomerism?

(a) 2-Butene

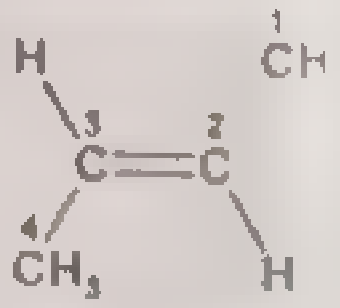
It will show geometrical isomerism since two different groups are attached to each C atom of double bond

$CH_3-CH=CH-CH_3$ $\Longrightarrow$

2-Butene



cis-2-Butene

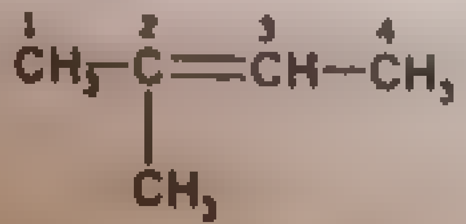


trans 2 Butene

2

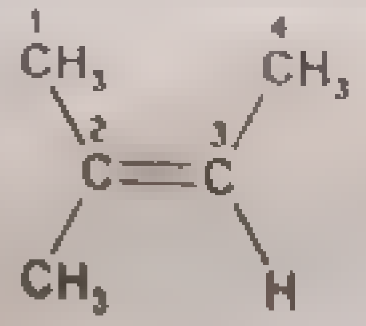
(b) 2-Methyl-Butene

It will not show geometrical isomerism since one carbon of double bond ...



2-Methyl 2-butene

$\Longrightarrow$



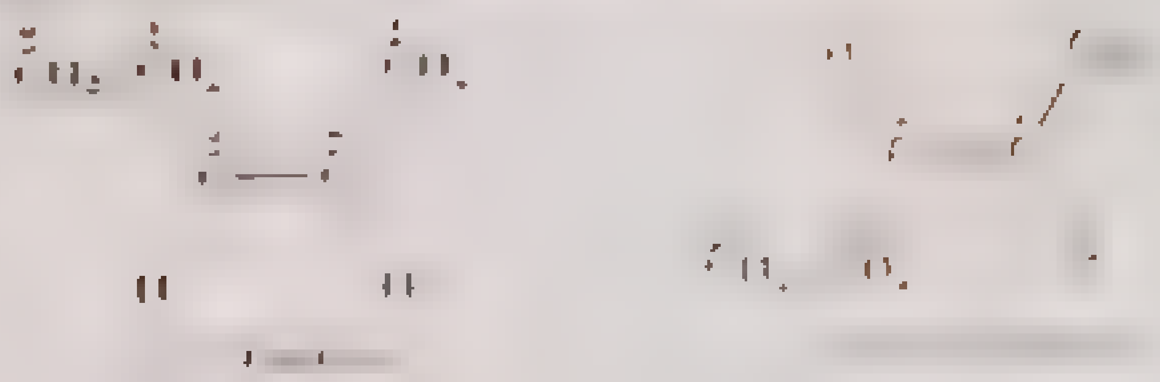
2-Methyl 2 butene

(c) **2 Pentene**

It will show geometrical isomerism [illegible]

$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H=\overset{2}{C}H-\overset{1}{C}H_3$ ⟶

2-Pentene



(d) **1,2-Dichloropropane**

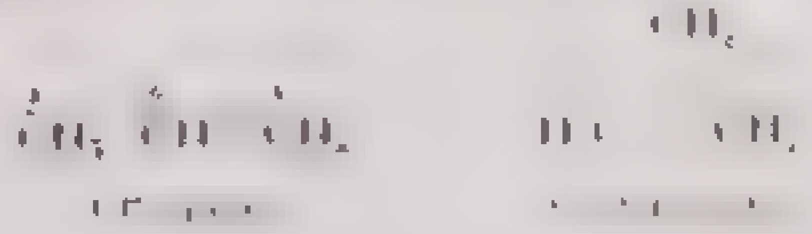
It will show geometrical [illegible]
cyclic ring

4. ***Which of the following compounds show isomerism?***

(a) [illegible]

- It will not show [illegible]
groups attached [illegible]
- It will not show optical [illegible]

NOTE [illegible]
different structures and properties [illegible]



(b) [illegible]

- It will not show optical [illegible]
- It will [illegible]
bond

... [illegible] ... isomers ...

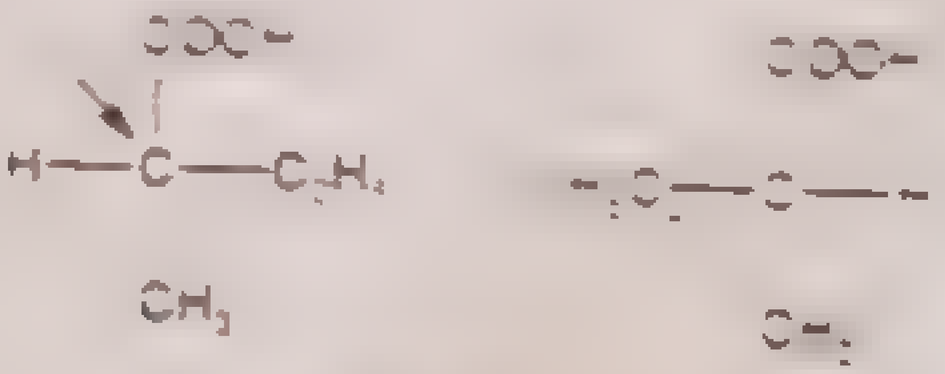
5 [illegible]

6 [illegible]

7 [illegible]

8 An acid of formula $C_5H_{10}O_2$ is optically active. What is its structure?

Asymmetric carbon



2-Methylbutanoic acid
Enantiomers

9 *How does cis-isomer convert into trans-isomer?*
Page 162

10 *The trans-isomer is more stable. Why?*
Page 163

$\Rightarrow C_nH_{2n-2}$ → [illegible]

ALKYNES

from the corresponding alk[illegible]

I.U.P.A.C. NOMENCLATURE

(1) The parent hydrocarbon is the continuous chain containing triple bond

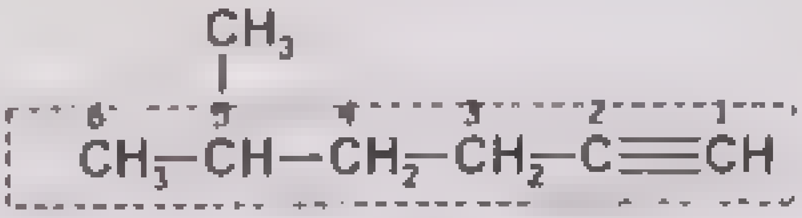
(2) The ending '**ane**' of the alkane is changed by **–yne**

$CH{\equiv}CH$

Ethyne

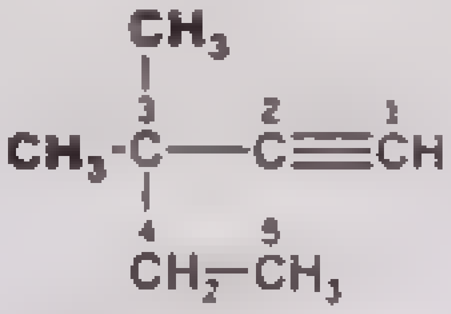
$CH_3{-}C{\equiv}CH$

Propyne



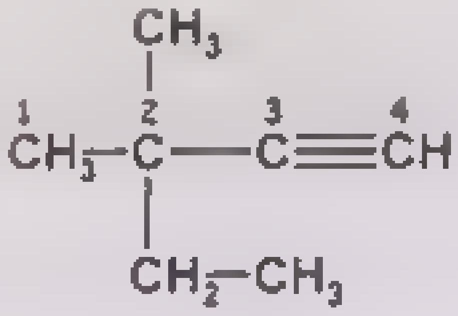
5-Methyl-1-hexyne

(3) The main chain is numbered starting from the terminal carbon nearer to the triple bond



3,3-Dimethyl-1-pentyne

(Correct)



(Incorrect)

(4) Triple bond is given the number of the lower carbon atom attached to triple bond separated by hyphen

$CH_3{-}CH_2{-}C{\equiv}CH$

1-Butyne

(5) If two or more triple bonds are there in the molecule use the prefixes di-, tri- etc

$\overset{6}{C}H{\equiv}\overset{5}{C}{-}\overset{4}{C}H_2{-}\overset{3}{C}H_2{-}\overset{2}{C}{\equiv}\overset{1}{C}H$

1,5-Hexadiyne

(6) Alkyl groups are indicated by the methods described while naming alkanes

NAMING OF MOLECULES CONTAINING BOTH THE DOUBLE AND TRIPLE BONDS

(1) The suffix 'ene' is used to denote the presence of Double bond

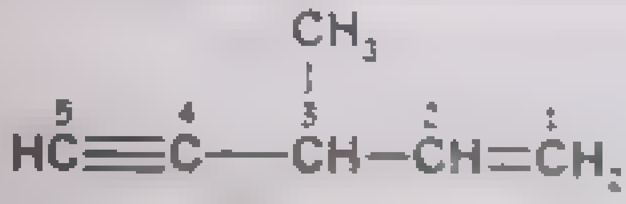
(2) the suffix –yne to denote the presence of triple bond

(3) The suffix –'**ene**' always precedes **yne** in the name of [illegible] even the double bond [illegible] the large number

(4) The position number for the double bond is placed between [illegible]

(5) The position number of triple bond is placed between [illegible]

(6) If same number would result from each terminal the double bond [illegible]



3-Methyl-1-penten-4-yne

$\overset{6}{C}H\equiv\overset{5}{C}-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

1-Hexen-5-yne

$\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H-\overset{6}{C}H_3$

4-Hexen-1-yne

$\overset{6}{C}H\equiv\overset{5}{C}-\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}H=\overset{1}{C}H_2$

1,3-Hexadien-5-yne

$\overset{6}{C}H\equiv\overset{5}{C}-\overset{4}{C}\equiv\overset{3}{C}-\overset{2}{C}H=\overset{1}{C}H_2$

1-Hexene-3,5-diyne

$\overset{6}{C}H\equiv\overset{5}{C}-\underset{\underset{CH_3}{|}}{\overset{4}{C}H}-\overset{3}{C}H_2-\overset{2}{C}H=\overset{1}{C}H_2$

4-Methyl-1-hexen-5-yne

$\overset{1}{C}H\equiv\overset{2}{C}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-\overset{4}{C}H=\overset{5}{C}H-\overset{6}{C}H_3$

3-Methyl-4-hexen-1-yne

ACTIVITY

Give the IUPAC name of the following

(a) $CH_3-C\equiv CH$

1-Propyne

(b) $\overset{4}{C}H\equiv\overset{3}{C}-\overset{2}{C}\equiv\overset{1}{C}H$

1,3-Butadiyne

(c) $H_2\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}\equiv\overset{4}{C}H$

1-Buten-3-yne

(d) $\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}\equiv\overset{4}{C}-\overset{5}{C}H=\overset{6}{C}=\overset{7}{C}H-\overset{8}{C}H_3$

5,6-octadiene-1,3-diyne

(e) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

3-Hexyne

RELATIVE STABILITY

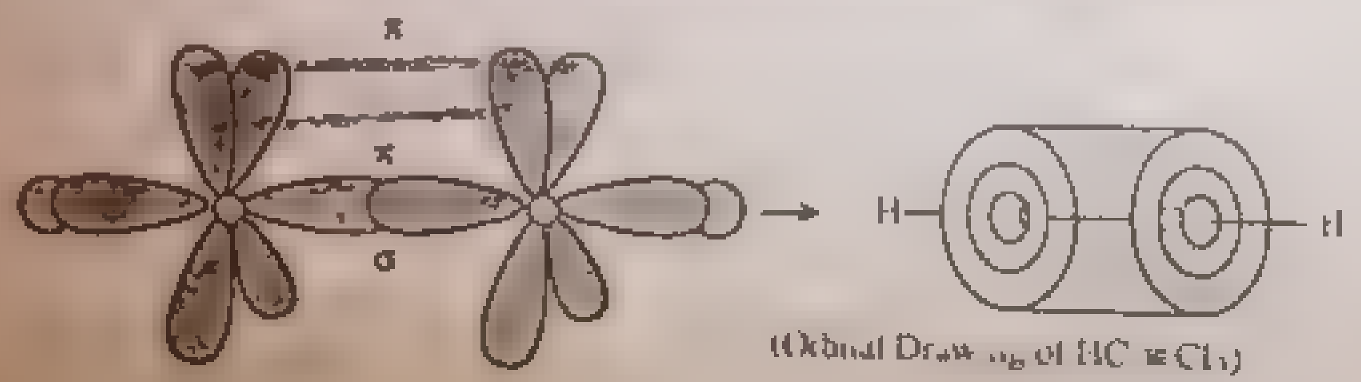
Alkynes are more stable as compared to alkenes due to the presence of extra pi bond. That is why alkynes are less reactive than alkene.

This can be supported by the thermodynamic data of alkynes and alkenes i.e.

ΔH of 1-Hexyne = 290 kJ/mol while ΔH of 1-Hexene = 126 kJ/mol. Thus, alkynes require more energy.

STRUCTURE

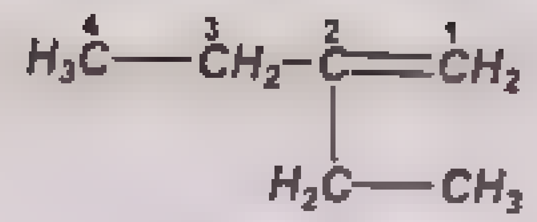
- The two carbons of acetylene (alkyne) are sp hybridized. They are linked by a sigma bond due to sp-sp overlap.
- The unhybridized two p-orbitals on one carbon overlap with two p-orbitals on other carbon to form pi-bonds.
- The cloud of pi-electrons is present cylindrically symmetrical about the carbon-carbon sigma-bond.



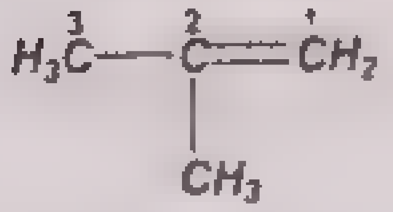
(Orbital Drawing of HC ≡ CH)

- Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is linear molecule and hence geometrical isomer is not observed in it.

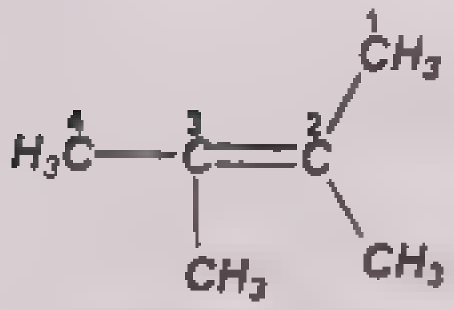
MORE PRACTICE



2-Ethyl-1-butene

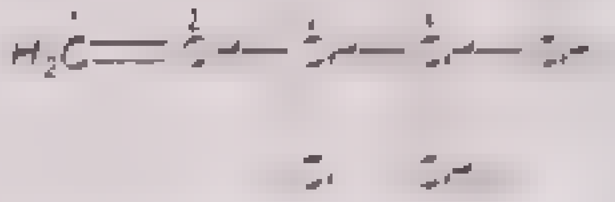


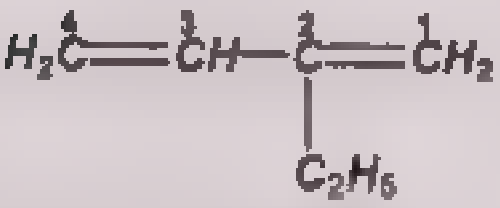
2-Methyl-1-propene



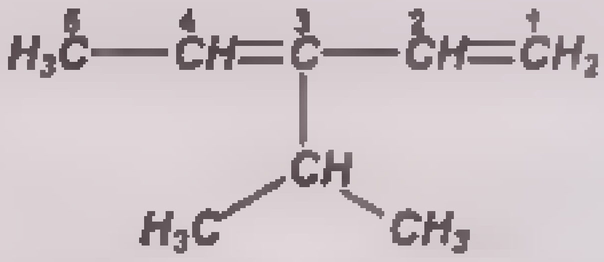
2 3-Dimethyl-2-butene

3-Chloro-1-propene

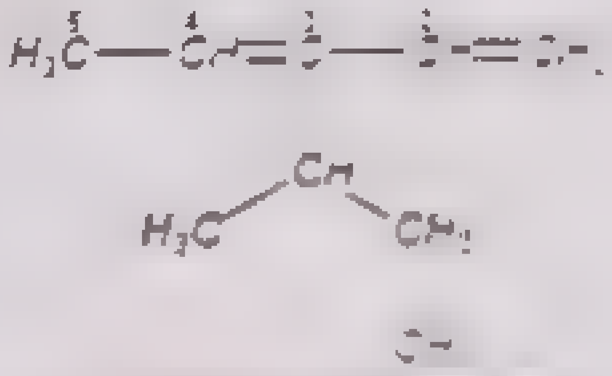


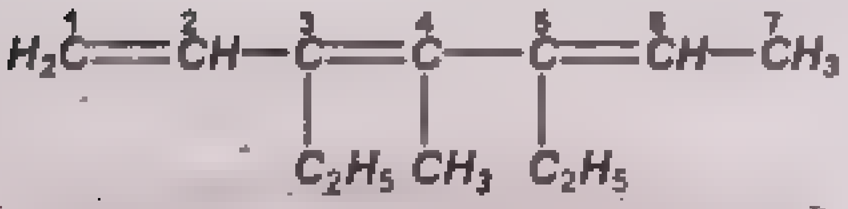


2-Ethyl-1,3-butadiene

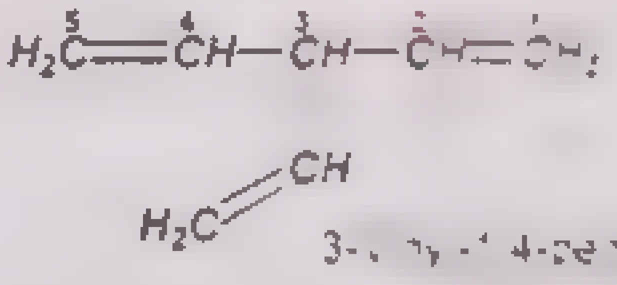


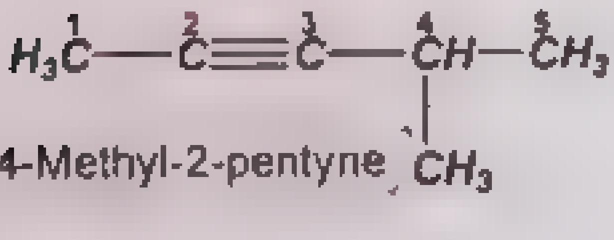
3-iso-propyl-1,3-pentadien



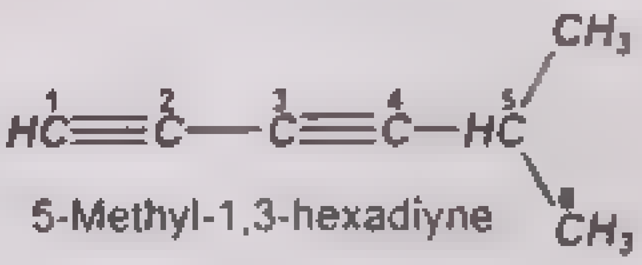


3 5-Diethyl-4-methyl-1,3,5-heptatriene



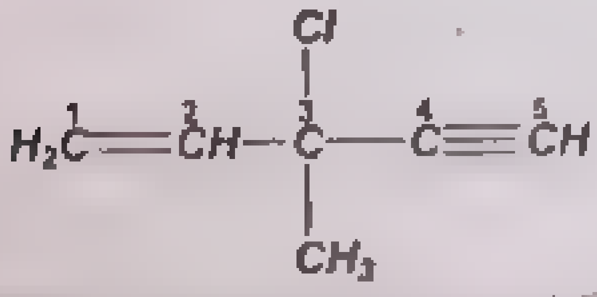


4-Methyl-2-pentyne

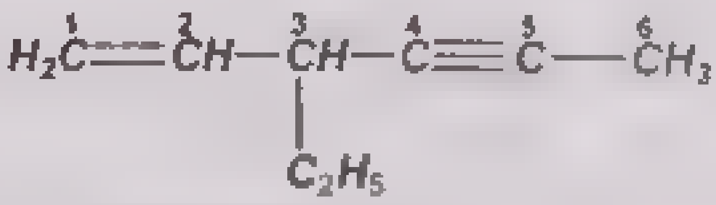


5-Methyl-1,3-hexadiyne

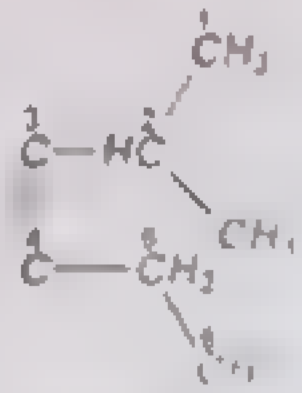
1-Penten-4-yne



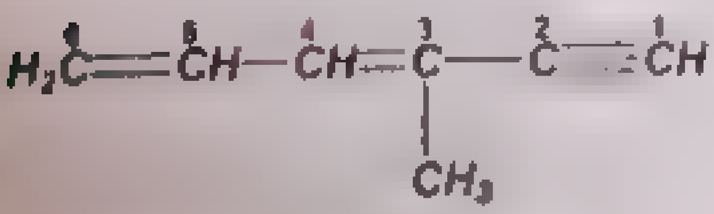
3-Chloro 3-methyl 1-penten 4 yne



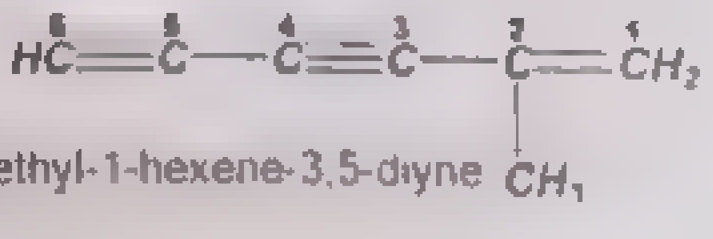
3 Ethyl 1 hexen-4-yne



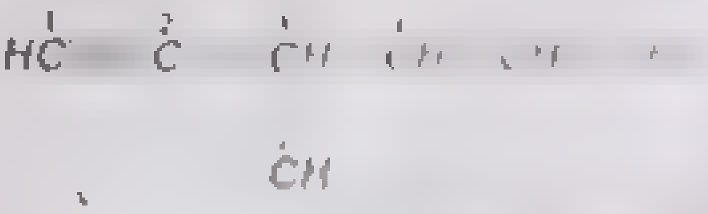
2 Methyl 3 hexyne



4-Methyl-1,3-hexadien-5-yne



2-Methyl-1-hexene-3,5-diyne



PHYSICAL PROPERTIES

In general alkynes are non polar and are insoluble in water but soluble in non-polar organic solvents

PREPARATION OF ALKYNES BY ELIMINATION REACTIONS

Alkynes can be prepared by the following methods

(i) Elimination reaction

(ii) Alkylation of sodium acetylide

(i) ELIMINATION OF HYDROGEN HALIDE (DEHYDROHALOGENATION):

The removal of hydrogen and halogen from a molecule is called dehydrohalogenation

Alkynes can be prepared by dehydrohalogenation of vicinal and geminal dihalides in the presence of alkaline reagents

(a) Dehydrohalogenation of Vicinal Dihalides

- A vicinal dihalide contains two halogen atoms on adjacent carbon atoms

1,2 dibromoethane alc KOH

$$\underset{\substack{|\quad\ \ |\\ Br\quad Br}}{CH_2-CH_2} \xrightarrow[-HBr]{Base} \underset{\substack{|\\ Br}}{CH=CH_2} \xrightarrow[-HBr]{Base} CH\equiv CH$$

- Higher alkynes are also formed in the presence of alcoholic KOH, e.g.,

$$\underset{\substack{|\qquad\ |\\ Br\quad\ Br}}{CH_3-CH_2-CH-CH_2} + 2KOH \xrightarrow[100\text{-}200\ ^\circ C]{alcohol} CH_3-CH_2-C\equiv CH + 2KBr + 2H_2O$$

1,2-dibromobutane 1-butyne

Q. How KOH can migrate

- In the presence of strong base such as KOH and at high temperature triple bond at ... to give more disubstituted alkyne

$$\underset{\text{1-Butyne}}{CH_3-CH_2-C\equiv CH} \longrightarrow \underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3}$$

Q How

- Therefore alcoholic KOH is useful when rearrangement is not possible

$$\underset{\substack{|\qquad\ |\\ Br\quad\ Br}}{C_6H_5-CH-CH-C_6H_5} + 2KOH \xrightarrow[100\text{-}200\ ^\circ C]{alcohol} C_6H_5-C\equiv C-C_6H_5 + 2KBr + 2H_2O$$

Q. How

- 1-alkynes can be prepared from vic-dihalides with sodium amide

$$\underset{\substack{|\qquad\ |\\ Br\quad\ Br}}{C_6H_5-CH-CH_2} + 3NaNH_2 \xrightarrow[-33\ ^\circ C]{liquid\ NH_3} C_6H_5-C\equiv C^-Na^+ + 2NaBr + 3NH_3$$

$$C_6H_5-C\equiv C^-Na^+ \xrightarrow{H_2O} C_6H_5-C\equiv CH$$

(a) Dehydrohalogenation of Geminal Dihalides

A dihalide containing two halogen atoms linked with the same carbon atom) on treatment with strong base gives alkyne, e.g.,

$$C_6H_5-CH_2-CHBr_2 + 3\,NaNH_2 \xrightarrow[-33\ ^\circ C]{liquid\ NH_3} C_6H_5-C\equiv C^-Na^+ + 2\,NaBr + 3\,NH_3$$

$$C_6H_5-C\equiv C^-Na^+ \xrightarrow{H_2O} C_6H_5-C\equiv CH$$

(II) ALKYLATION OF SODIUM ACETYLIDE

The sodium salt of alkyne can be reacted with an alkyl halide to give bigger alkyne

$$C_6H_5-C\equiv C^-Na^+ + \overset{\delta+}{CH_3}-\overset{\delta-}{Br} \longrightarrow C_6H_5-C\equiv C-CH_3 + NaBr$$

REACTIVITY

- Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions
- It also undergoes substitution reactions due to easy cleavage of C-H bond

The pi-electrons are present cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon-carbon boding. Thus electrophilic substitution reactions are possible in acetylene and 1-alkyens (terminal alkynes)

(A) – ACIDITY OF TERMINAL ALKYNES

The acidic hydrogen of alkynes can be removed by a base (

$$R-C\equiv C-H + B:^- \longrightarrow R-C\equiv C^- + B-H$$

- In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atoms with s-sp overlap
- An sp hybrid orbital has 50% s-character in it and makes the carbon atoms more electronegative. Thus the sp-hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$H-\overset{\delta-}{C}\equiv C-\overset{\delta+}{H}$$

- This $H^{\delta+}$ can be substituted with metal. Thus substitution reaction occurs due to $H^{\delta+}$

Examples:

(i) When 1 alkyne or ethyne is treated with sodamide in liquid ammonia ... passed ... of acetylides are obtained

$$R-C\equiv CH + NaNH_2 \xrightarrow{liquid\ NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2\,Na \longrightarrow Na^+\,C^-\equiv C^-\,Na^+ + H_2$$

Sodium acetylide is a very valuable reagent for chemical syn...

(ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution chloride and silver nitrate respectively

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Red ppt.}}{CuC\equiv CCu} + 2NH_4Cl + 2$$

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{White ppt}}{AgC\equiv CAg} + 2NH_4NO_3 + 2$$

Thus, these reaction can be used to detect 1 alkynes (*terminal alkynes*)

- Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC\equiv CAg + H_2SO_4\,_{(dilute)} \longrightarrow HC\equiv CH + Ag_2SO_4$$

$$AgC\equiv CAg + H_2NO_3\,_{(dilute)} \longrightarrow HC\equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification separation, and identification of alkynes

(B) ADDITION REACTIONS OF ALKYNES

- Alkynes undergo addition reactions just like alkenes
- The high electron density of the π-bonds makes them nucleophilic.
- Two factors influence the relative reactivity of alkynes compared to alkenes:
  (i) increased nucleophilicity of the starting p system, and
  (ii) stability of any intermediates (for example carbocations)

(1) HYDROGENATION

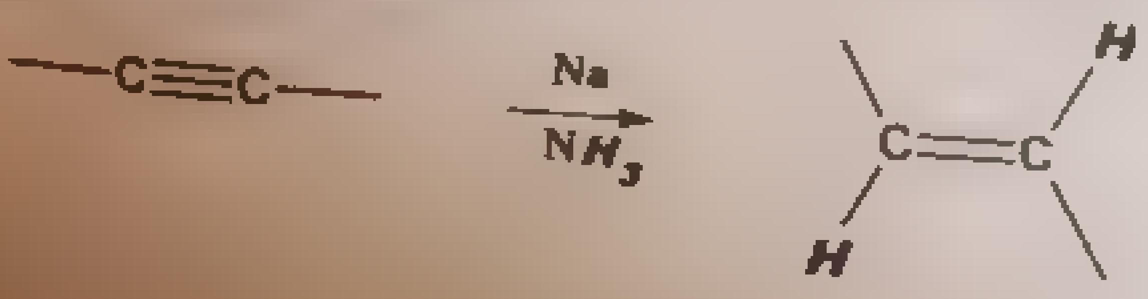
- Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or P
- In the first step alkenes are formed which them take up another molecule of hydrogen to form an alka

$$CH\equiv CH + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} CH_2=CH_2$$

$$H_2C=CH_2 + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} CH_3-CH_3$$

(2) DISSOLVING METAL REDUCTION

Alkynes can be reduced to *trans*-alkenes using Na in NH_3 (liq.)



Remember!
syn-addition

- This reaction is stereoselective because it gives only the *trans*-alkene via an *anti* addition.
- The reaction proceeds via single electron transfer from the Na with H coming from the NH_3
- The stereochemistry of this reaction is opposite to that of catalytic hydrogenation (*syn*-addition)
- These reaction conditions do not reduce alkenes, hence the product is the alkene

(3) HYDROHALOGENATION

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes. The reaction occurs in accordance with Markownikov's rule

$$CH\equiv CH + H-Br \longrightarrow \underset{\text{Vinyl bromide}}{CH_2=CH-Br}$$

Second addition is according to Markownikov's Rule

$$CH_2=CH-Br + H-Br \longrightarrow \underset{\text{1,1 Dibromoethane}}{CH_3-CH(Br)_2}$$

(4) HYDRATION

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid.

$$CH\equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} \underset{\text{Vinyl alcohol}}{CH_2=CH-OH}$$

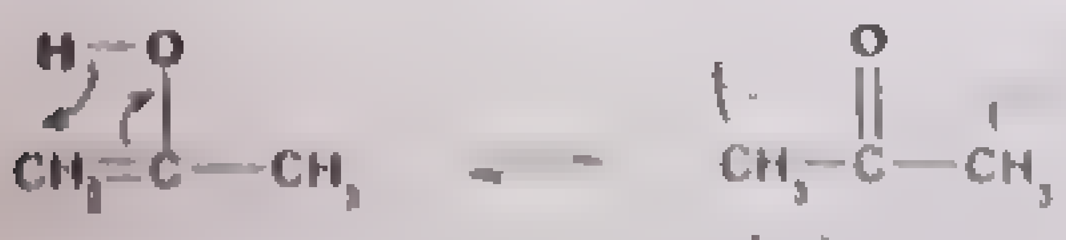
Rearrangement of Alcohol:

Vinyl alcohol is unstable. It has the hydroxyl group attached to a double bonded carbon ... to acetaldehyde

Acetaldehyde

$$CH_3-C\equiv CH + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_2SO_4]{HgSO_4} CH_2=C(OH)-CH_3$$

1 - propyne



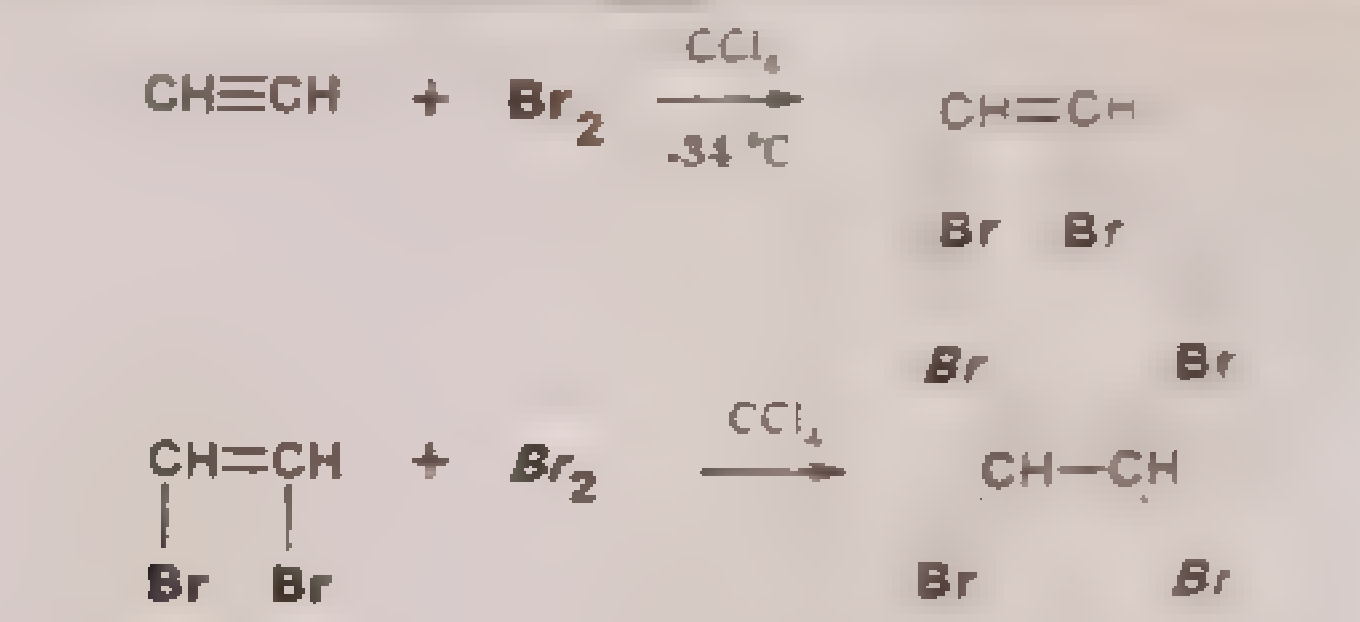
Acetone

This reaction is industrially important because aldehydes can be prepared by

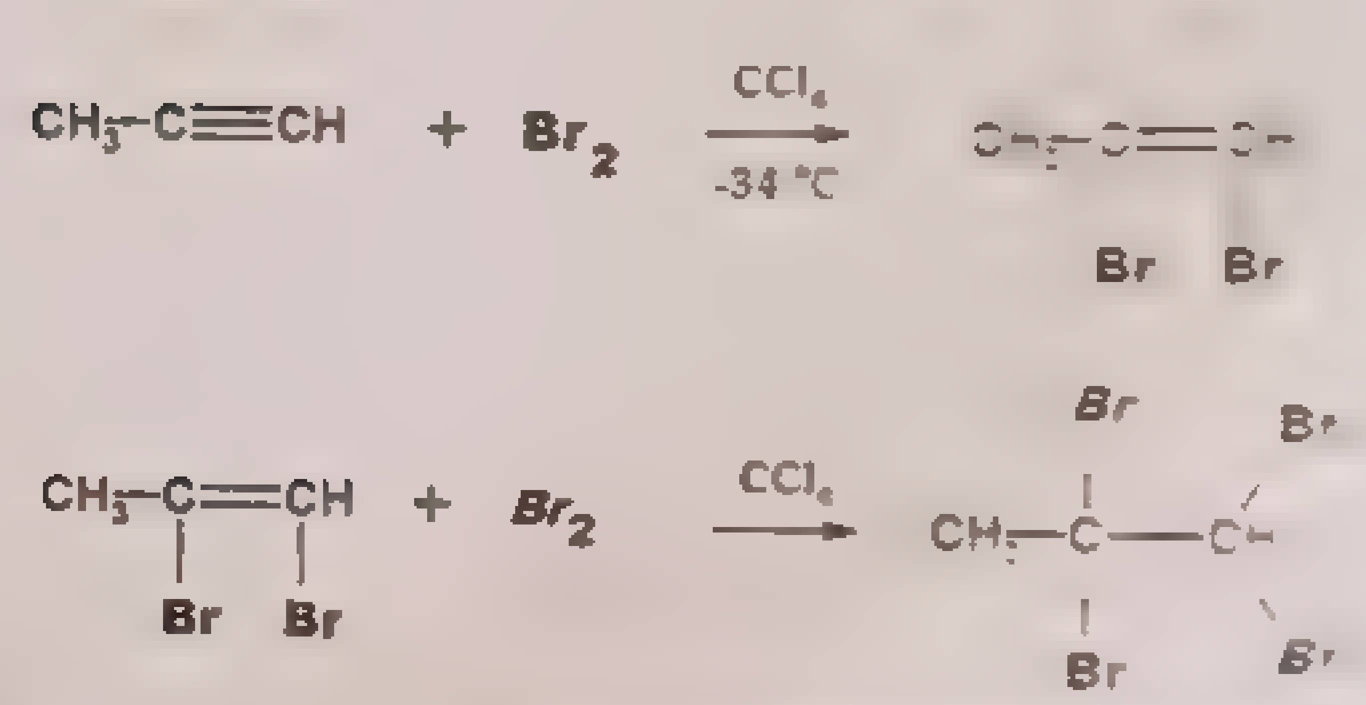
(5) BROMINATION

Chlorine and bromine add to the

(i)



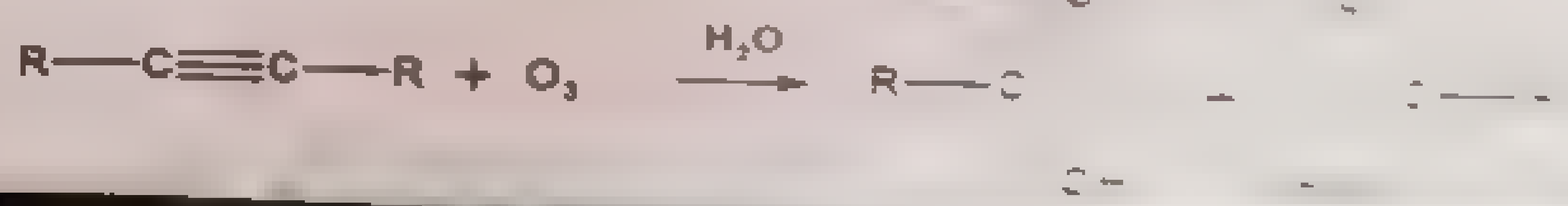
(ii)



The Halogenation may be stopped at the dihaloalkene
less nucleophilic than even triple bond itself

(6) OZONOLYSIS

When ozone reacts with alkyne followed by aqueous work up

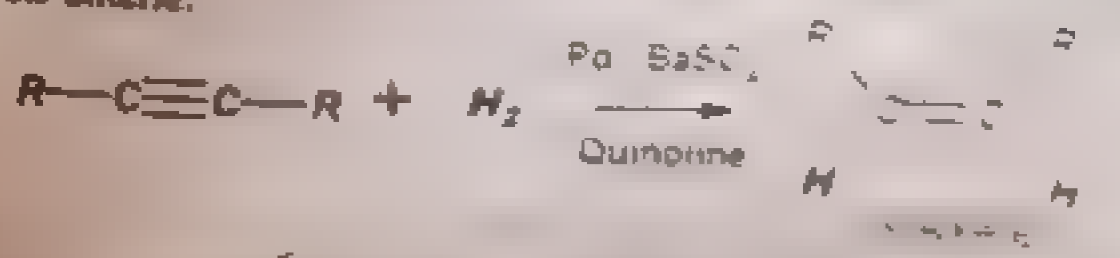


QUICK QUIZ-5

What are reducing agent would you use to convert an alkyne to

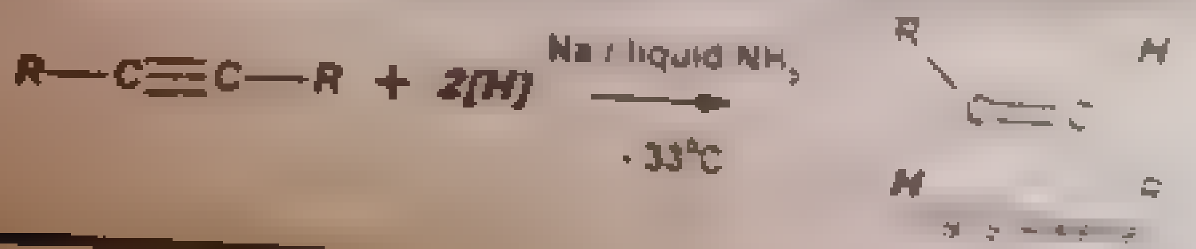
(i) cis-Alkene

The catalyst is finely divided Pd supported on
The product is cis-alkene.



(ii) trans-Alkene

It can also be done by treating alkynes with Na



SOME IMPORTANT CONVERSIONS

(i) Methane to Ethane.

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight}} H_3C-Cl + HCl$$

$$2\ H_3C-Cl + 2\ Na \xrightarrow{\text{ether}} H_3C-CH_3 + 2\ NaCl$$

(ii) Ethyl chloride to ethene.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} + KOH \xrightarrow{\text{alcohol}} \underset{\text{Ethene}}{H_2C=CH_2} + KCl + H_2O$$

(iii) Ethene to ethyl alcohol

$$\underset{\text{Ethylene}}{H_2C=CH_2} + \underset{\text{Sulfuric acid}}{H-OSO_3H} \longrightarrow \underset{\text{Ethyl hydrogen sulfate}}{CH_3-CH_2-OSO_3H}$$

$$CH_3-CH_2-OSO_3H + H_2O \xrightarrow{100^\circ C} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + H_2SO_4$$

(iv) Ethene to ethyne

$$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{H_2C}-\underset{Br}{CH_2}$$

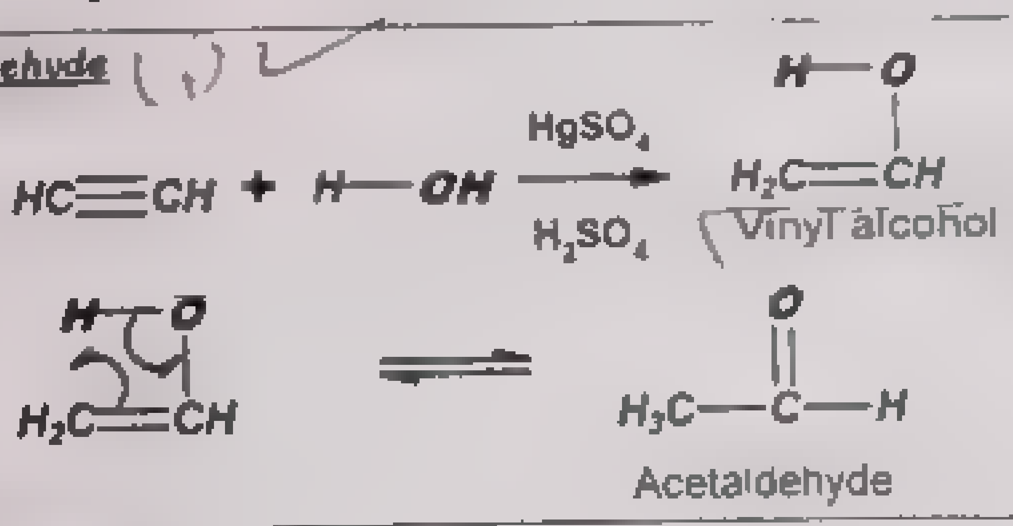
$$\underset{Br}{H_2C}-\underset{Br}{CH_2} + 2\ KOH \xrightarrow{\text{Alcohol}} HC\equiv CH + 2\ KBr + 2\ H_2O$$

(v) Ethane to Ethene

$$H_3C-CH_3 + Cl_2 \xrightarrow{\text{sunlight}} H_3C-CH_2-Cl + HCl$$

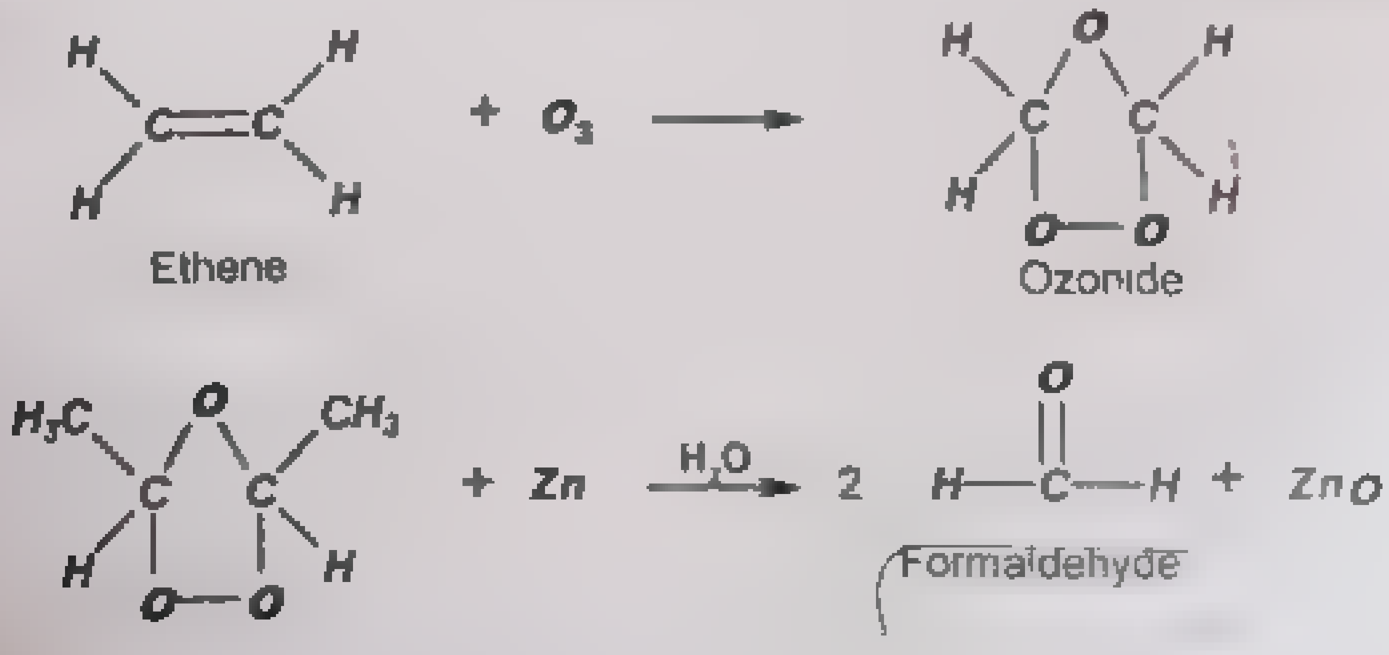
$$H_3C-\underset{Cl}{CH_2} + KOH \xrightarrow{\text{alcohol}} H_2C=CH_2 + KCl + H_2O$$

(vi) Ethyne to Acetaldehyde



Similarly Propyne to Acetone

(vii) Ethene to formaldehyde



BENZENE AND SUBSTITUTED BENZENES

Important Information

Discovered by:	Michael Faraday
Isolated by:	Hoffmann from
Molecular Formula	C_6H_6
Molecular weight	78 g mol^{-1}
Special Features	*(i)* Resonance *(ii)* Electrophilic Substitution Reactions

- Michael Faraday discovered benzene in 1825 during the destructive distillation of vegetable oil
- Hoffmann isolated it from coal tar
- As a functional group, benzene and substituted benzenes are called ***arenes***

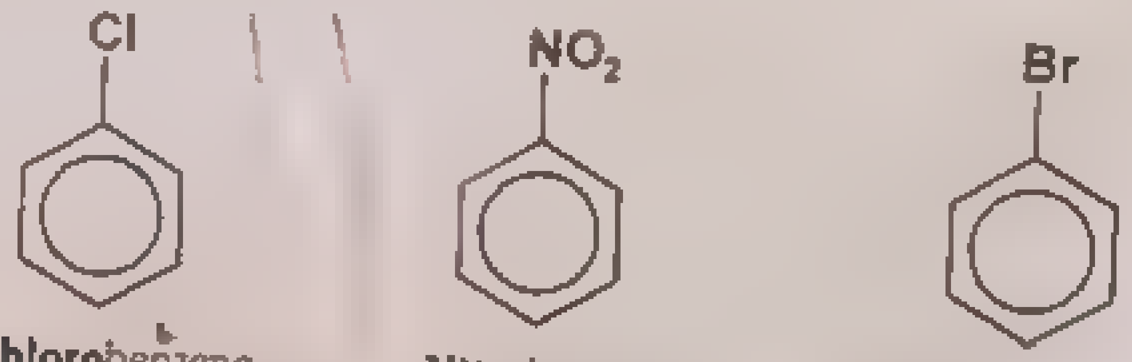
NOMENCLATURE:

MONOSUBSTITUTED BENZENES

(a) Common System Naming:

The following procedures are adopted for naming *mono-substituted benzenes*

(1) Parent name is benzene and the substituent is indicated by a prefix, **e.g.**



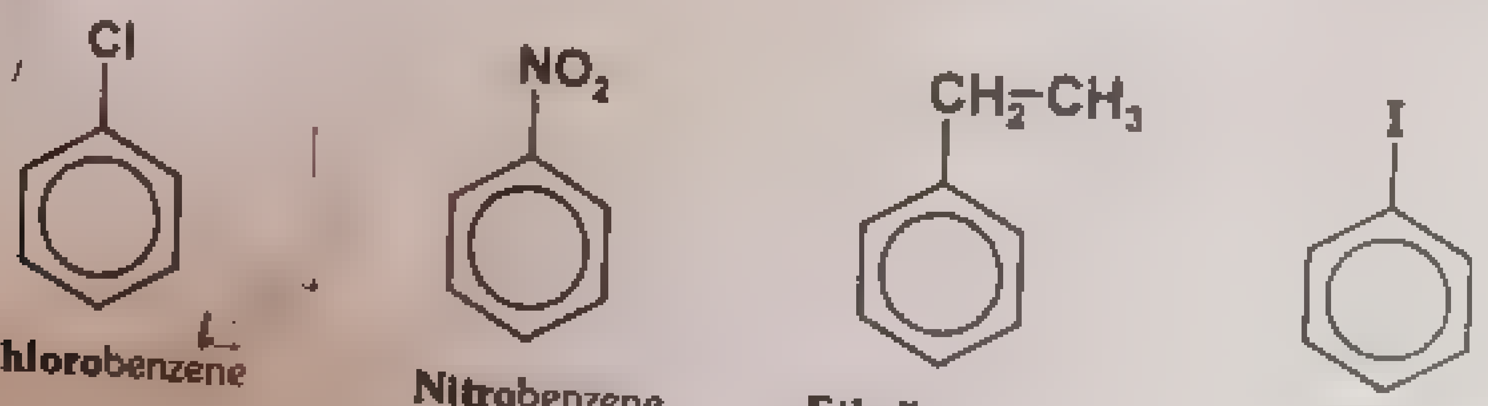
Chlorobenzene **Nitro**benzene **Bromo**benzene

(2) The substituent and the benzene ring taken together may form a new parent name. The largest parent is preferred **e.g.**, $C_6H_5CH_3$ may be named as. *(i)* Methyl benzene, *(ii)* Phenyl methane. According to "largest rule" methyl benzene is preferred. (*Since benzene is the larger parent than methane*)

(b) IUPAC System of Naming:

(1) Mono-substituted derivatives of benzene are named by prefixing the name of substituted to the 'benzene'

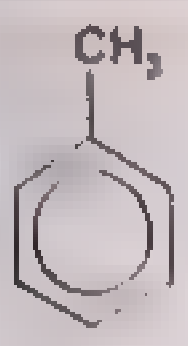
Example:



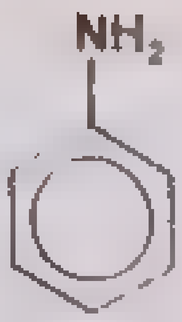
Chlorobenzene **Nitro**benzene **Ethyl**benzene **Iodo**benzene

(2) Many aromatic compounds have been known by their common or trivial names which are still in use. I.U.P.A.C. system retains these names

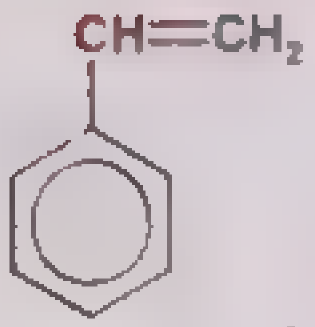
A few are given below:



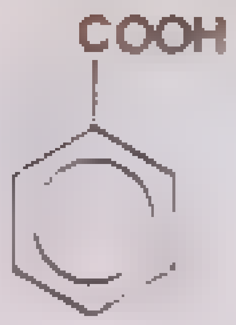
Toluene



Aniline

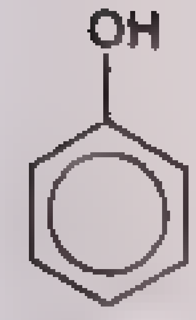


Styrene

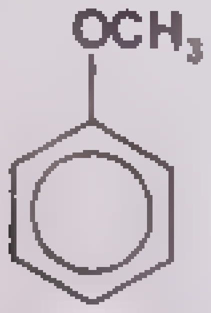


Benzoic acid

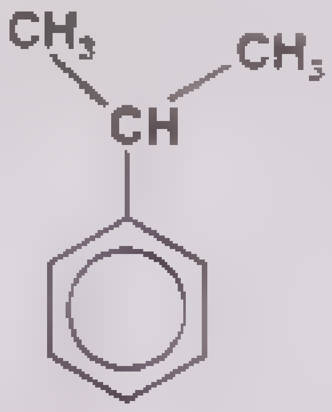
Benzaldehyde



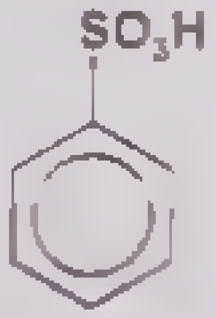
Phenol



Anisole



Cumene



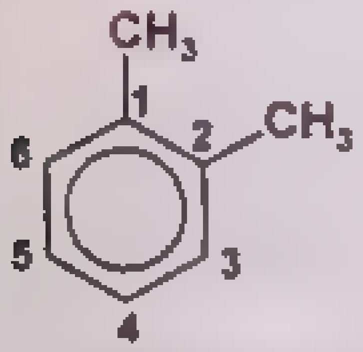
Benzenesulfonic acid

Acetophenone

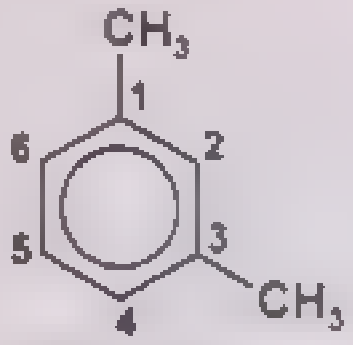
DISTRIBUTED BENZENE

(1) When there are two substituents on benzene ring their relative positions are indicated

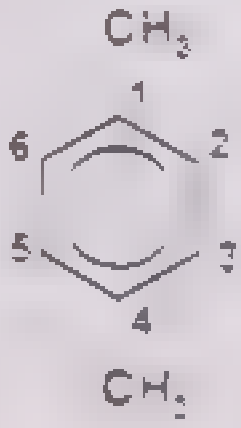
- by prefixes ortho (*o*), meta (*m*) and para (*p*) in common system of naming and
- by numerals while naming according to IUPAC system



o-Dimethylbenzene
(1,2-Dimethylbenzene)
(o-Xylene)

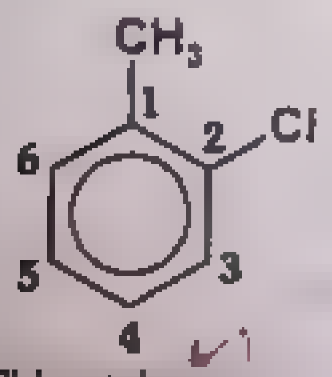


m-Dimethylbenzene
1,3-Dimethylbenzene
(m-Xylene)

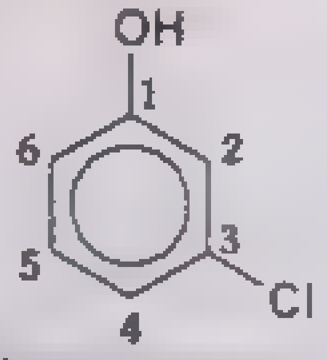


(2) If the substituents are different and one of them is an alkyl group, the numbering ... carbon which is linked to the alkyl group and the second substituent ...

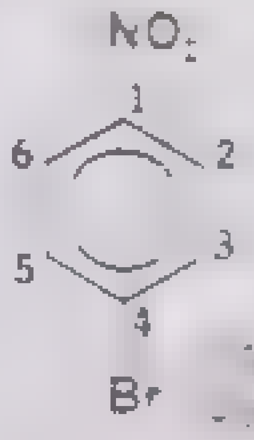
(3) When a common name is used, the substituent which is responsible for the name e.g. ... in phenol, is considered to be on carbon-1. Thus numbering is started from the ... group and such a compound is named as derivative of the parent ...



o-Chlorotoluene or
2-Chlorotoluene (IUPAC)

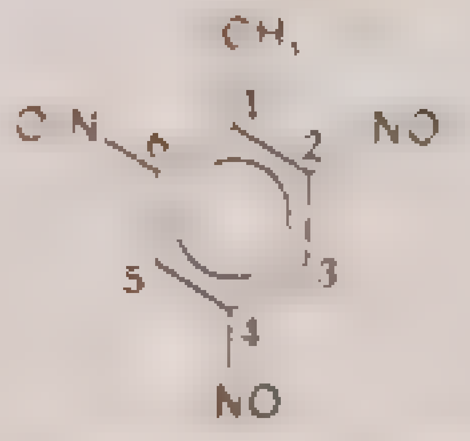


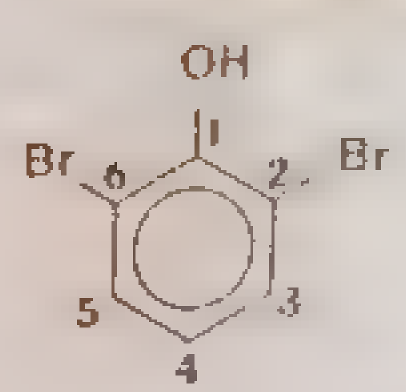
m-Chlorophenol or
3-Chlorophenol ...



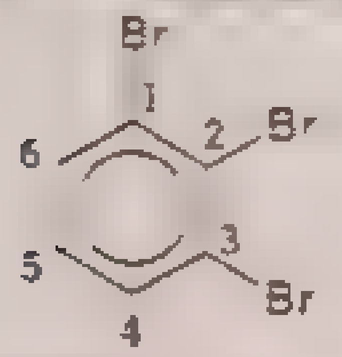
(4) When two substituents are different, they are used ...

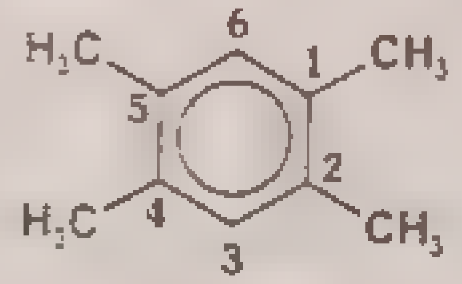
(5) Poly-substituted benzenes are named by numbering ... lowest possible numbers. The last named substituent ... not indicated in the name





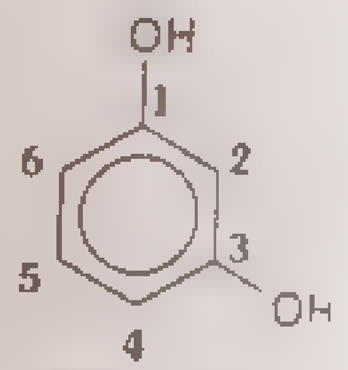
6 ... are named by numbering the substituents ...



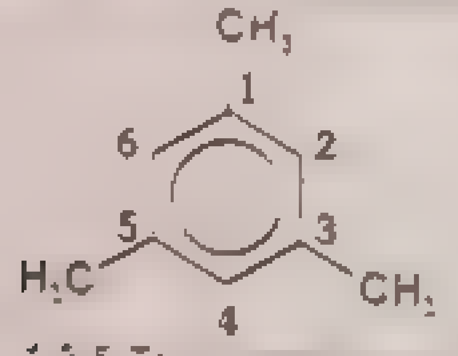


Durene or

1,2,4,5-Tetramethylbenzene (IUPAC)

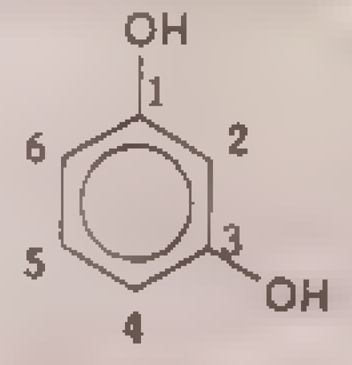


7 Some ... benzenes ... by their common name

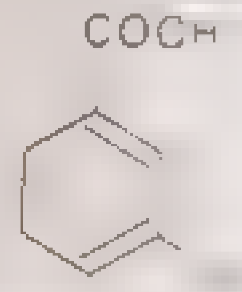


1,3,5-Trimethylbenzene

Mesitylene



Resorcinol



Remember!

If two different functional groups are present on benzene ring then ... is better ... Example

–CN , –CHO , –COCH₃ , –OH , –NH₂ , –OR , –R The group ...

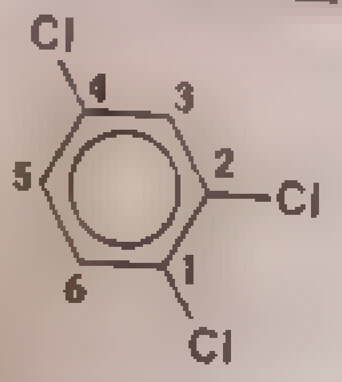
COOH and OH are present, then COOH ... high priority, and the compound ...

ACTIVITY:-

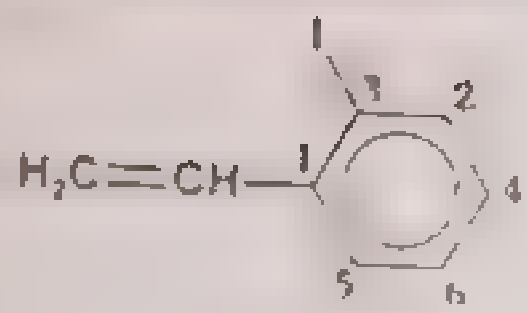
1- Give the suitable name to each of following:-

(a) 

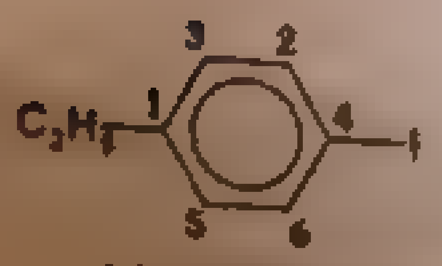
Chlorobenzene

(b) 

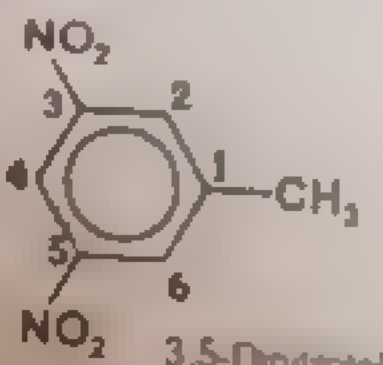
1,2,4-Trichlorobenzene

(c) 

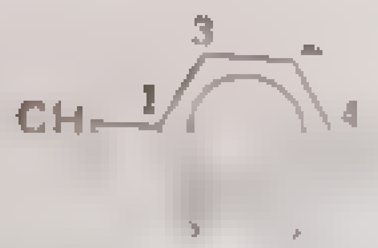
(d)

(e) 

1-Ethyl-4-iodobenzene

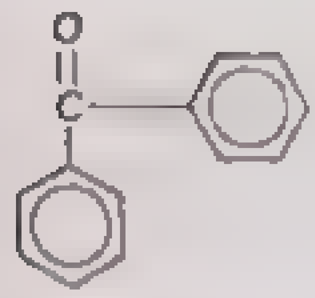
(f) 

3,5-Dinitrotoluene

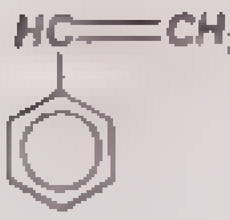
(g) 

MORE PRACTICE

AROMATICS

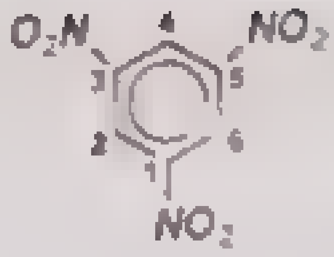


Benzophenone



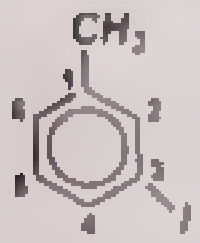
Vinylbenzene

4-Methylbenzoic acid

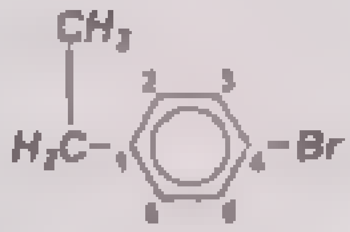


1,3,5-Trinitrobenzene

2-Hydroxyacetophenone

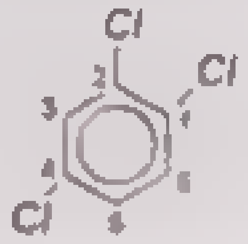


3-Iodotoluene

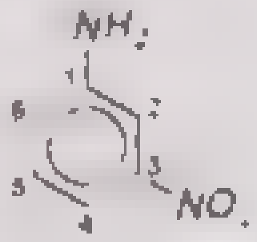


4-Bromoethylbenzene

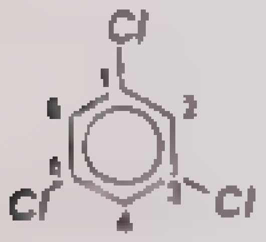
3-Aminobenzoic acid



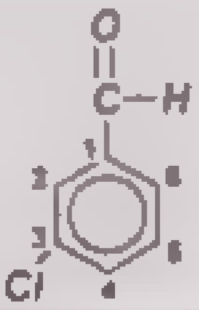
1,2,4-Trichlorobenzene



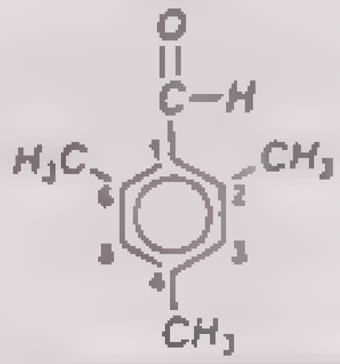
3-Nitroaniline



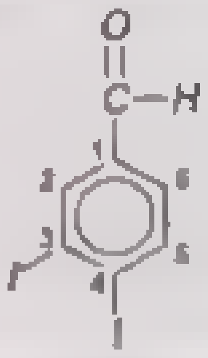
1,3,5-Trichlorobenzene



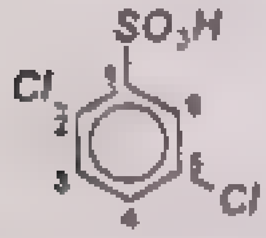
3-Chlorobenzaldehyde



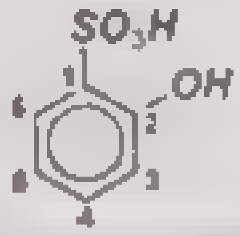
2,4,6-Trimethylbenzaldehyde



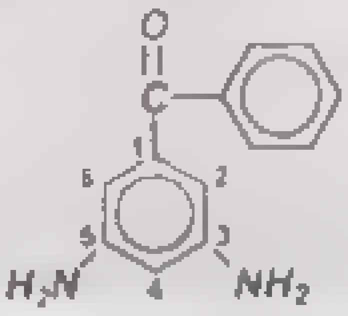
3,4-Diiodobenzaldehyde



2,5-Dichlorobenzenesulfonic acid

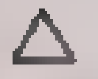


2-Hydroxybenzenesulfonic acid

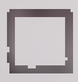


3,5-Diaminobenzophenone

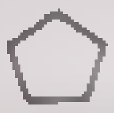
CYLCLIC



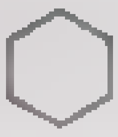
cyclopropane



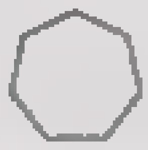
cyclobutane



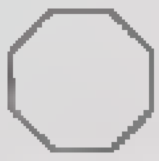
cyclopentane



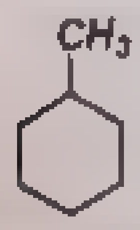
cyclohexane



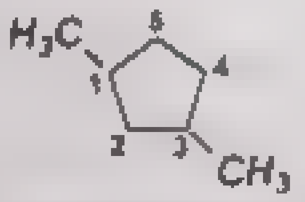
cycloheptane



cyclooctane

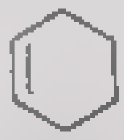


Methylcyclohexane

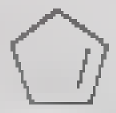


1,3-Dimethylcyclopentane

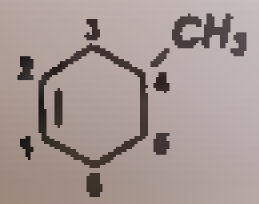
Methylcyclopropane



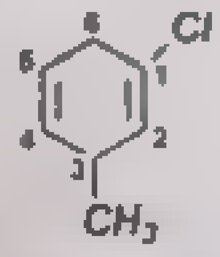
cyclohexene



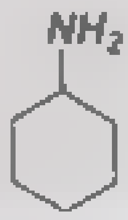
Cyclo-1,3-pentadiene



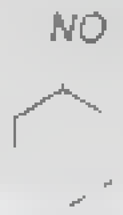
4-Methylcyclohexene



1-Chloro-3-methylcyclohexa-1,4-diene



Cyclohexanamine

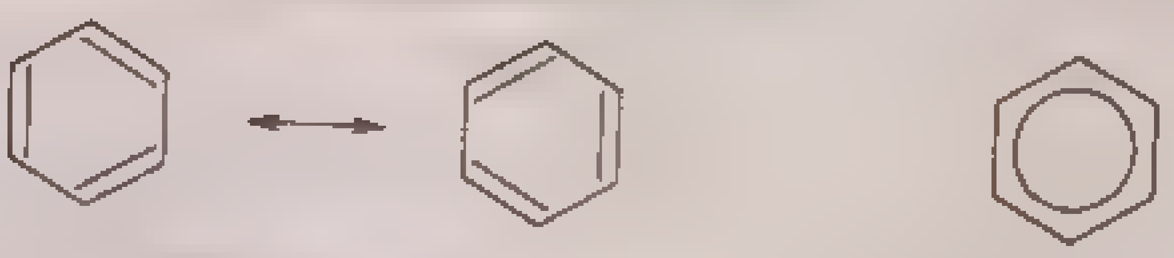


Nitrocyclohexane

PHYSICAL PROPERTIES:

In the absence of polar substituents [illegible] hydrocarbons. [illegible] are non polar, have low melting [illegible] boiling points and low solubility in polar solvents.

STRUCTURE (MOLECULAR ORBITAL ASPECTS)



Kekule structures Robinson structure

- All twelve atoms in benzene (C_6H_6) [illegible] same plane.
- Benzene has a planar, cyclic [illegible] structure.
- It contains alternating C=C and C-C bonds. Thus two different Kekule structures are obtained. These two equally valid resonance contributors.
- Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.
- All the CC bonds are **1.4 Å** [between typical C=C (**1.33 Å**) and C-C (**1.54 Å**) distances]

Which representation is best?

- In benzene all the CC bonds are known to be of equal length, so there are no C=C and C-C. This is represented by the resonance hybrid in the Robinson form.
- However, the key to organic chemistry is to understand mechanisms and draw curved arrows to show positions of the electrons. The Kekule structures give a more precise description of the electron positions.
- **Hence, it is a good idea to use a Kekule representation**

Limitations of Kekule's Structure

Kekule's structure failed to explain as to why

(1) Benzene is less reactive

(2) It shows dual character, i.e., it shows addition as well as substitute reaction

(3) It has less heat of formation, and

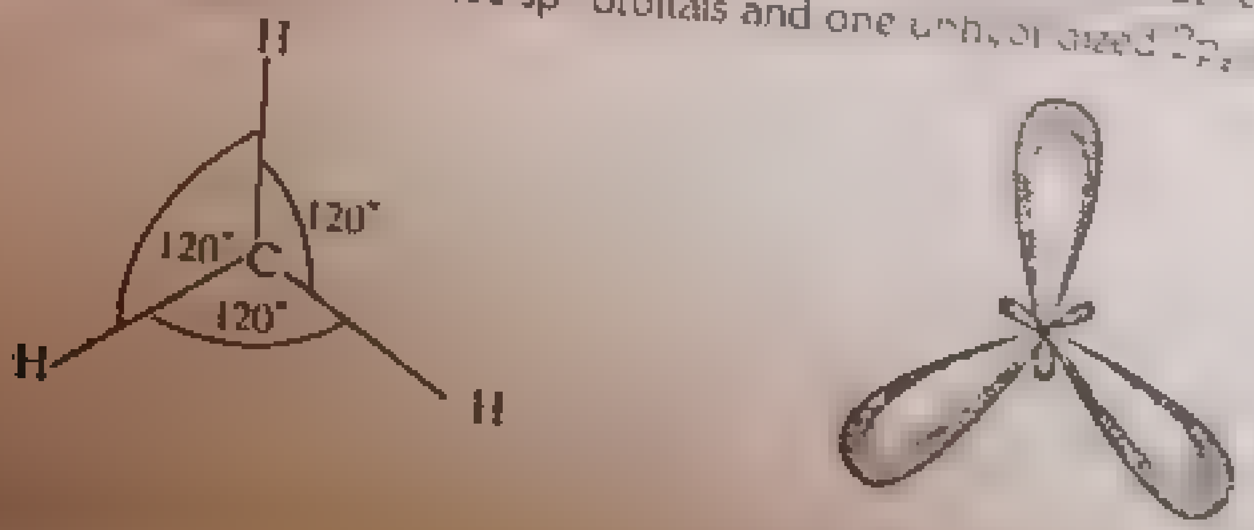
(4) It has equal C-C bonds

Exercise Q3 (4) (b). Explain the structure of benzene according to atomic orbital structure (or Molecular Orbital Structure).

MOLECULAR ORBITAL TREATMENT OF BENZENE (or ATOMIC ORBITAL TREATMENT)

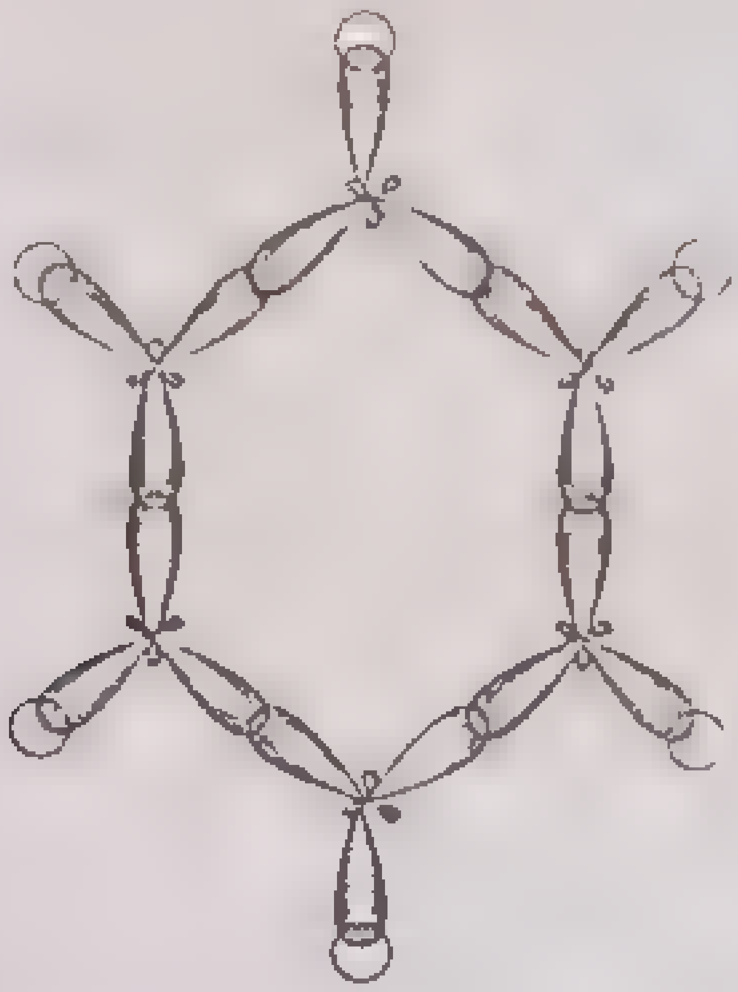
- Spectroscopic studies and X-rays analysis have shown that benzene is a regular, flat, planar hexagon [illegible]
- All six hydrogen atoms are co-planar with six carbon atoms.
- The bond angles are

  (i) C-C-C=120°, and *(ii)* C-C-H=120°
- Thus each C-atom is in a state of sp^2 hybridization because each C atom is attached to three [illegible]
- Each sp^2 hybridized carbon atom has three sp^2 orbitals and one unhybridized $2p_z$ [illegible]



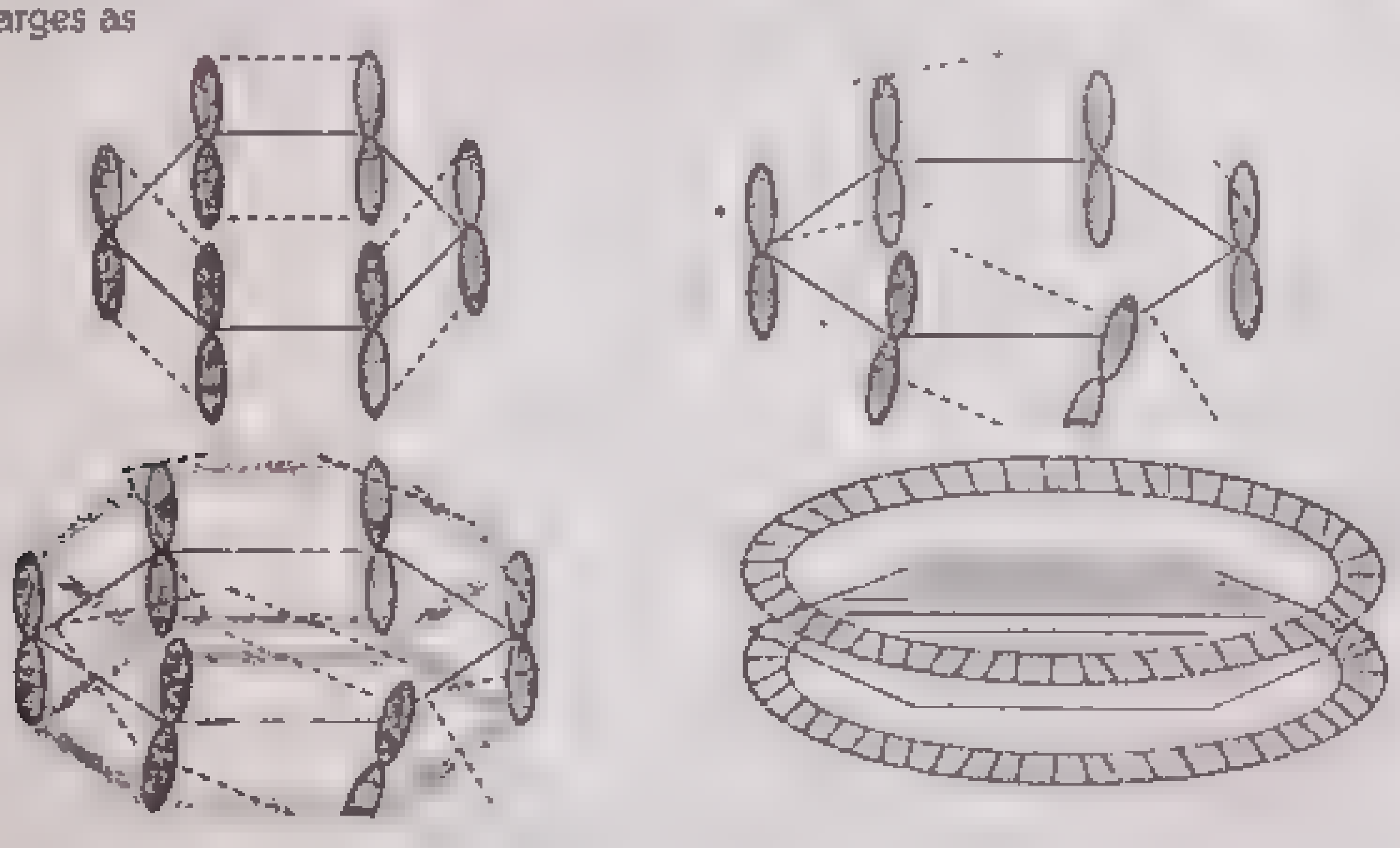
Sigma Framework of benzene.

The combination of six sp^2-hybridized carbon atoms and overlap of [illegible] following sigma frame work of benzene



Delocalized pi-bonding:

- Six atomic p-orbitals one on each C-atom are present perpendicular to the sigma bonding
- Each p-orbital overlaps in parallel manners with neighbouring p-orbitals to give a continuous sheath of negative charges as



Conclusions:

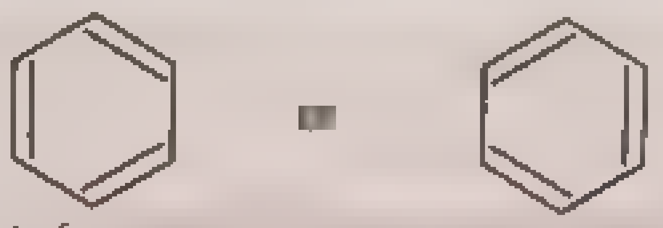
- The parallel overlap all six p-orbitals form an extensive delocalized pi-bonding [illegible] carbon nuclei of benzene
- Delocalization of p-orbitals over the entire ring produces sandwich like structure [illegible] the energy of molecule. Thus, the molecule becomes more stable and less reactive

Q. Why Benzene shows substitution [illegible]

- According to this molecular orbital picture each carbon carbon bond [illegible] one full sigma-bond and half a pi-bond. Thus, the carbon-carbon bond lengths are equal [illegible] benzene shows substitution as well as addition reactions

QUICK QUIZ-6

Criticize the following statement: *Benzene is a mixture of molecules most of which have the structure*



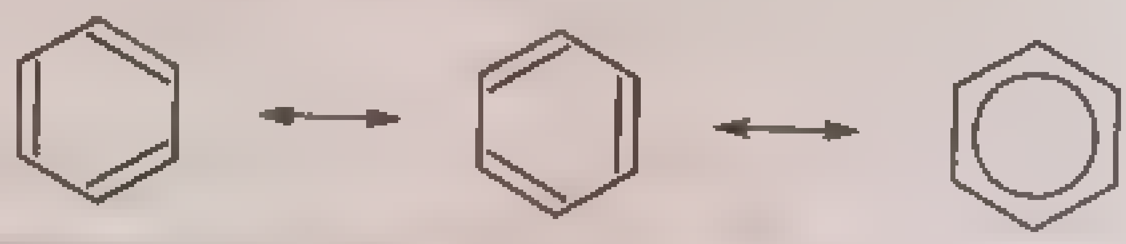
These two structures explain most of the experimental properties of benzene. So, it can be said that if ben... a mixture of molecules than most of these have the above structures.

However, these structures show that benzene contains double bonds, therefore, it should give reacti... unsaturated hydrocarbons i.e. addition reactions. However, benzene mostly gives substitution react... saturated hydrocarbons. Hence, these two are not actual structures of benzene. These can be consid... hypothetical structures.

MODERN REPRESENTATION OF BENZENE

With the help of molecular orbital behaviour we conclude that benzene has

- A regular hexagonal structure with an inscribed circle.
- A hexagon has alternate double and single bonds.



RESONANCE, RESONANCE ENERGY AND STABILIZATION

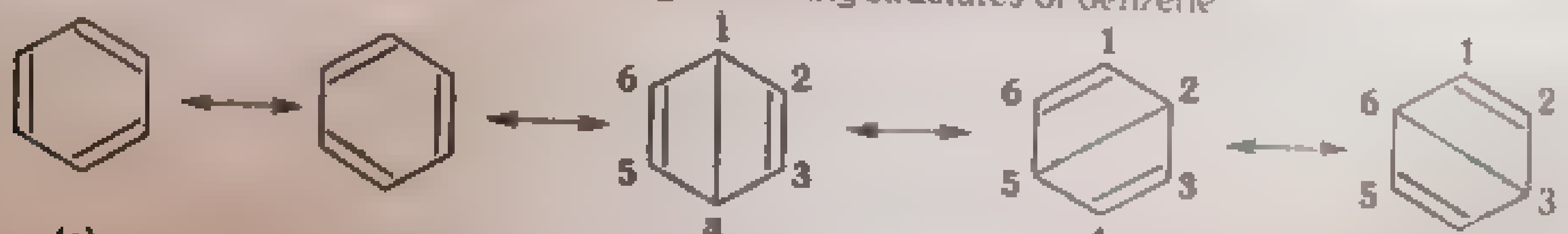
(I) RESONANCE

"The possibility of different pairing schemes of valence electrons of atom is called resonance" a... different structures thus arranged are called "Resonance Structures".

Explanation:

The resonance is represented by a double-headed arrow.

Example: The following different pairing schemes of the fourth valence (the p-electrons... possible in benzene. This gives the following resonating structures of benzene.



(a) (b) (c) (d) (e)

- The structures (a), (b) were proposed by Kekule and (c), (d), (e) were proposed by Dewar.
- The stability of a molecule increases with increase in the number of its resonance structures. Thu... of benzene is chemically quite stable.
- The actual structure of benzene is a resonance hybrid of all five structures.
- The Kekule's structure have the larger contribution and Dewar's structures have the... Therefore, benzene molecule can be represented by either of the two Kekule's structure.

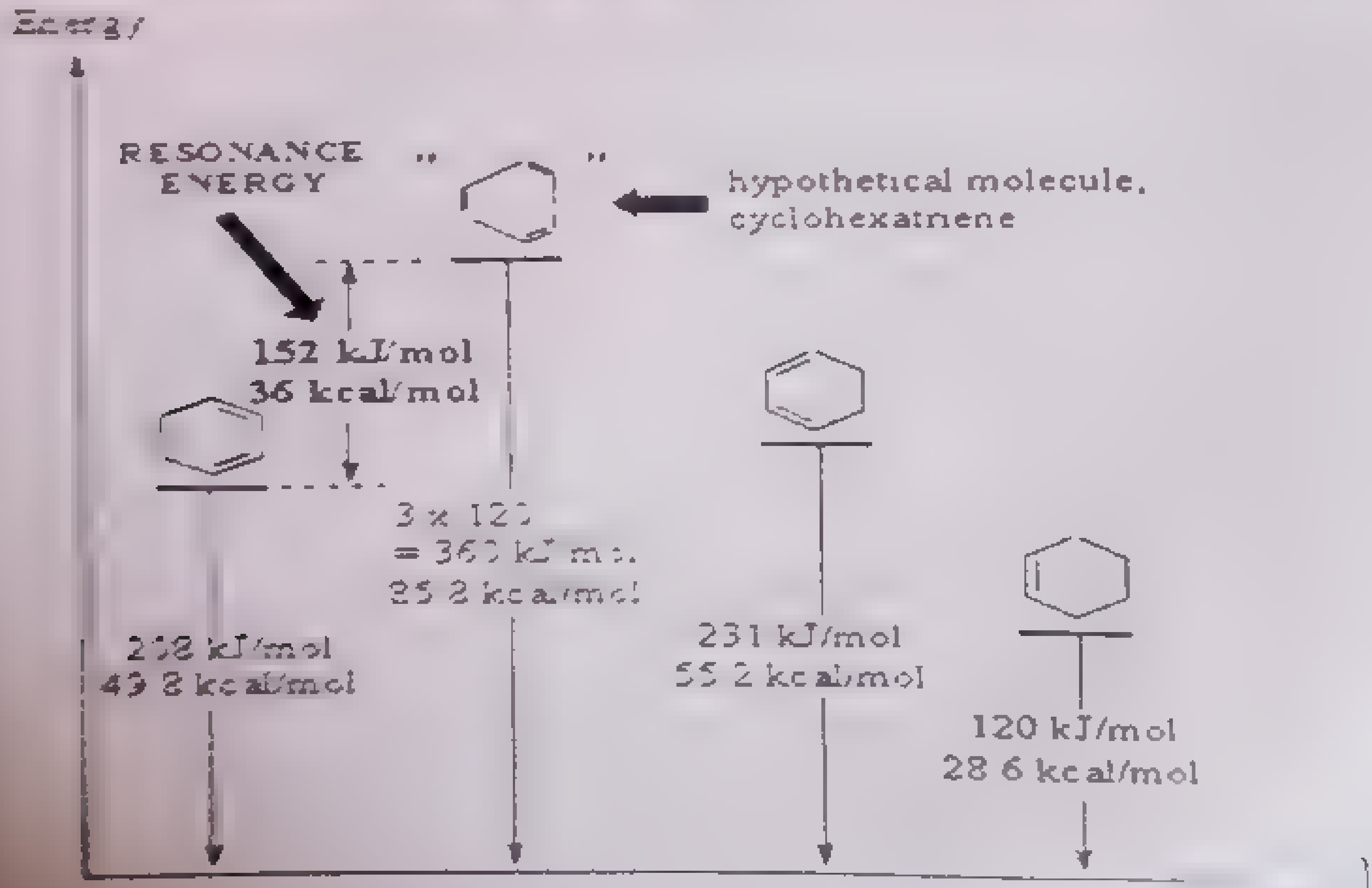
- The three alternate single and double bonds in the above structure are called conjugate bonds or resonating bonds
- Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal. However, these bonds are different from those in alkanes, alkenes and alkynes. It is intermediate between those in alkanes and alkenes
- The resonating single and double bonds in benzene can better be represented as follows

RESONANCE ENERGY

The resonance energy of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds. It can be calculated from experimental measurements

Explanation

- The diagram shows the experimental heats of hydrogenation, (ΔH_h) for three molecules, benzene, 1,3-cyclohexadiene and cyclohexene
- Under appropriate conditions they can all be reduced to the same product, cyclohexane
- The ΔH_h for cyclohexene is 120 kJ/mol
- In hypothetical cyclohexatriene molecule, the double bonds are assumed to be isolated from each other. Thus its ΔH_h should be three times of ΔH_h for cyclohexene (120 × 3=360 kJ/mol). Thus, during hydrogenation of hypothetical alkene 360 kJ/mol energy should be released from three isolated C=C bonds
- However, the experimental ΔH_h for benzene is 208 kJ/mol
- So, the difference between experimental value for benzene and that of hypothetical cyclohexatriene is 152 kJ/mol (360 − 208 = 152 kJ or 36 kcal/mol)
- Thus benzene is 152 kJ/mol ***more stable*** than the hypothetical system. This is the resonance energy for benzene



the more red ... area the higher
density ... blue
the electron density
area the lower the ... density

REACTIVITY AND REACTIONS

The image shows the electrostatic potential for benzene

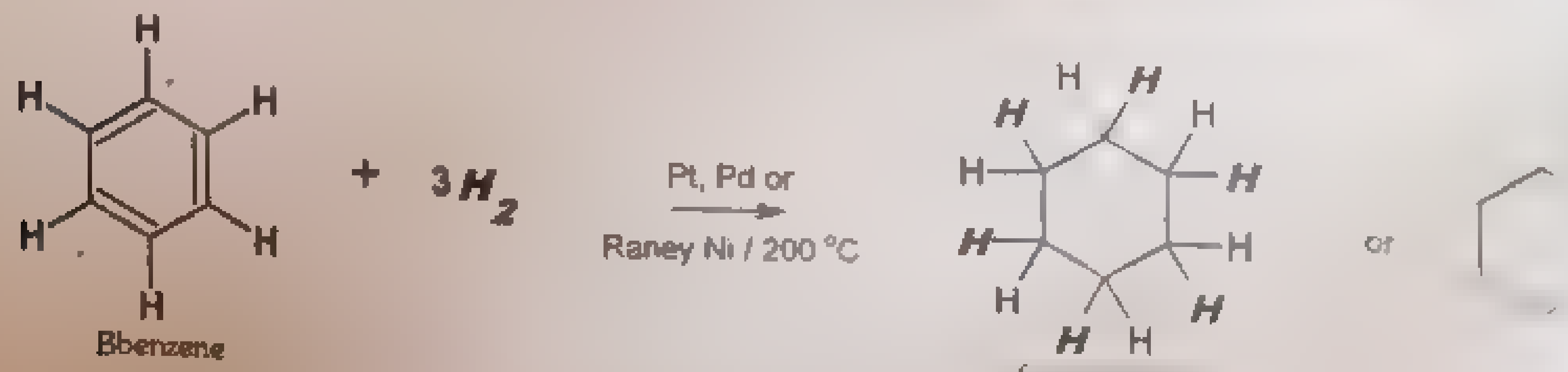
- The more dark area is the region of higher electron density and the less dark area is the region of lower electron density.
- Hence, the aromatic p-system is nucleophilic in character
- For arenes, there are two types of reactions
  - ✓ Reactions of electrophiles directly on the aromatic ring, and
  - ✓ Reactions of the substituents (since the neighboring aromatic group influences its reactivity)
- For reactions directly on the aromatic ring
  - ✓ The cyclic array of p-bonds is a region of high electron density so arenes are typically ... alkenes and alkynes)
  - ✓ Alkenes and alkynes undergo addition reactions. However, arenes typically undergo subs... which a group (usually -H) is replaced and the aromatic system is retained
  - ✓ The stability of the aromatic system favours substitution over addition. It is because addition ... the aromatic system

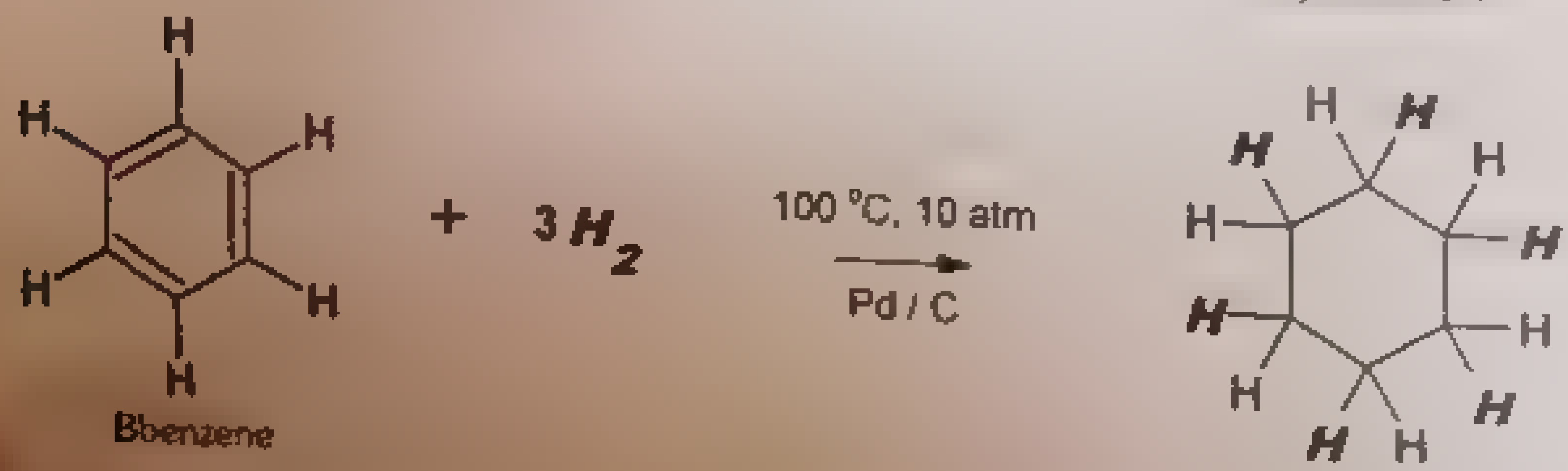
(A) ADDITION REACTIONS

- Benzene is highly unsaturated compound. It has three double bonds in it. But it does not ... reaction happily. The reason is that it shows resonance. The delocalization of pi electrons ...
- So for addition reaction benzene requires more vigorous condition than that of alkenes ...

(1) CATALYTIC HYDROGENATION

- Benzene can be hydrogenated in the presence of a catalyst as Pt, Pd or Raney ... temperature and pressures
- If we use the metals like Ru, Rh, supported at carbon then hydrogen ...

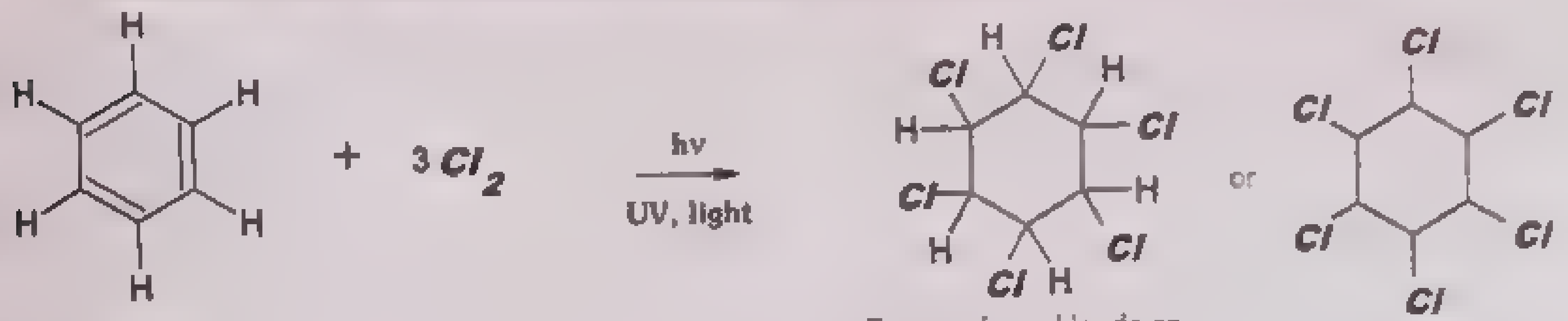




Cyclohexane

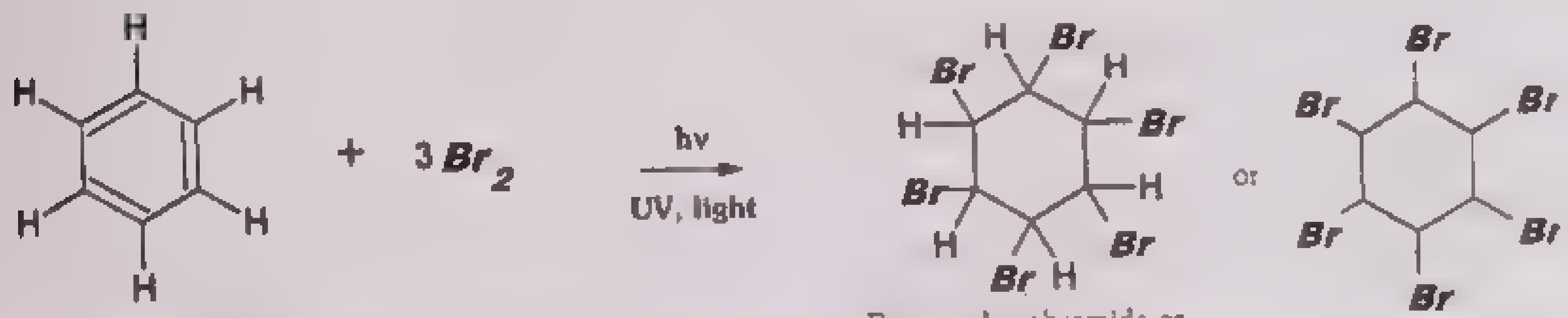
2) ADDITION OF HALOGENS

- Benzene can add three molecules of chlorine or bromine under the influence of light
- The benzene ring becomes saturated and we get benzene hexachloride and benzene hexabromide
- This reaction shows that benzene has three double bonds in the ring



Bbenzene

Benzene hexachloride or 1,2,3,4,5,6-Hexachlorocyclohexane



Bbenzene

Benzene hexabromide or 1,2,3,4,5,6-Hexabromocyclohexane

Reaction of F_2 and I_2:

The reaction of F_2 with benzene is very vigorous, while with I_2 it is very slow

Conclusion:

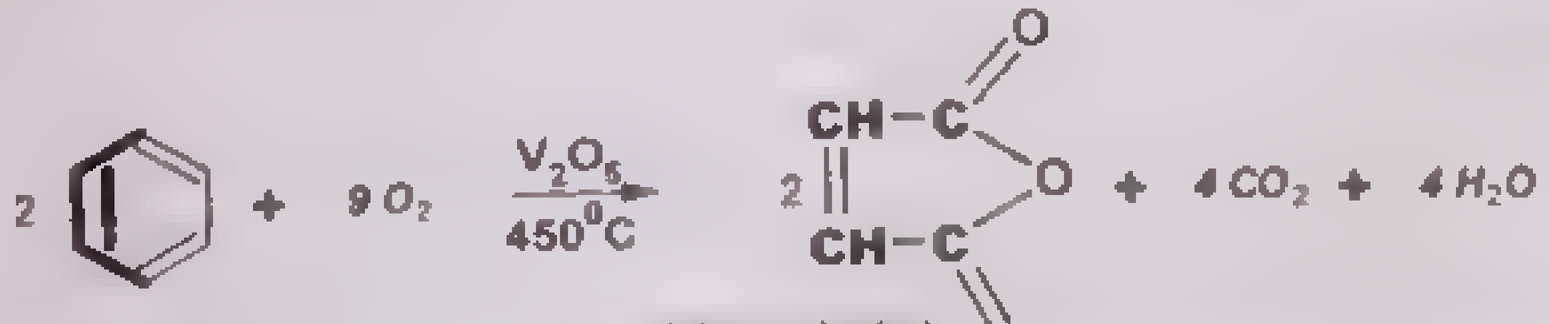
The addition reaction of hydrogen and chlorine show that benzene is unsaturated hydrocarbon and has three double bonds in it

(B) – OXIDATION REACTIONS

- *Benzene is stable towards general oxidizing agents. However, it can be oxidized under certain conditions*

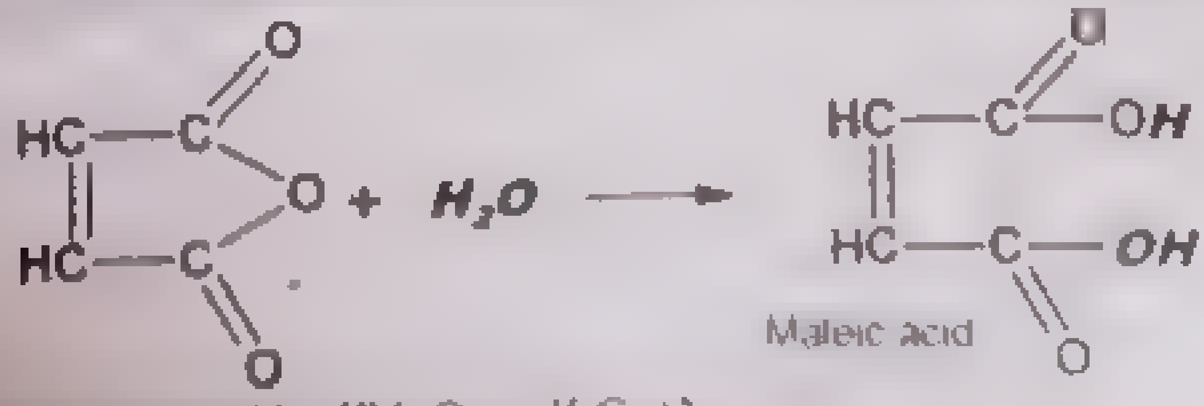
(1) CATALYTIC OXIDATION

When benzene is oxidized with air in the presence of V_2O_5 at 450°C, then we get maleic anhydride



Maleic anhydride

- This is commercial method for the preparation of maleic anhydride which on hydrolysis gives maleic acid



Maleic acid

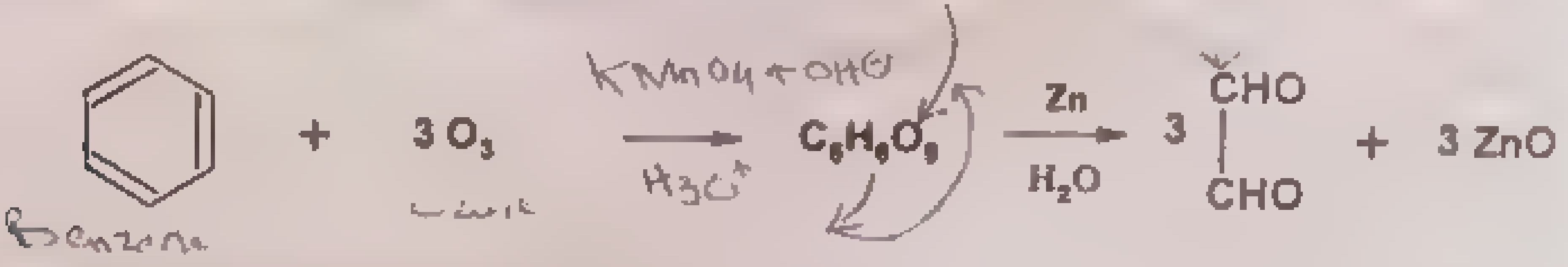
- Benzene is not oxidized by $KMnO_4$ or $K_2Cr_2O_7$

(2) COMBUSTION

When benzene is burnt in the presence of air or oxygen, CO_2 and H_2O are produced, just like other hydrocarbons

(3) OZONOLYSIS

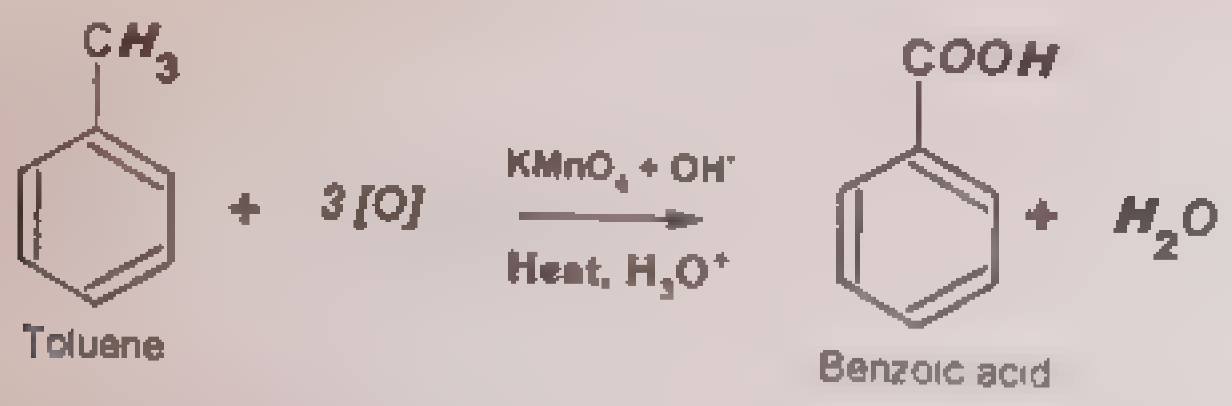
Benzene reacts with ozone and gives glyoxal, First of all triozonide is produced as an intermediate

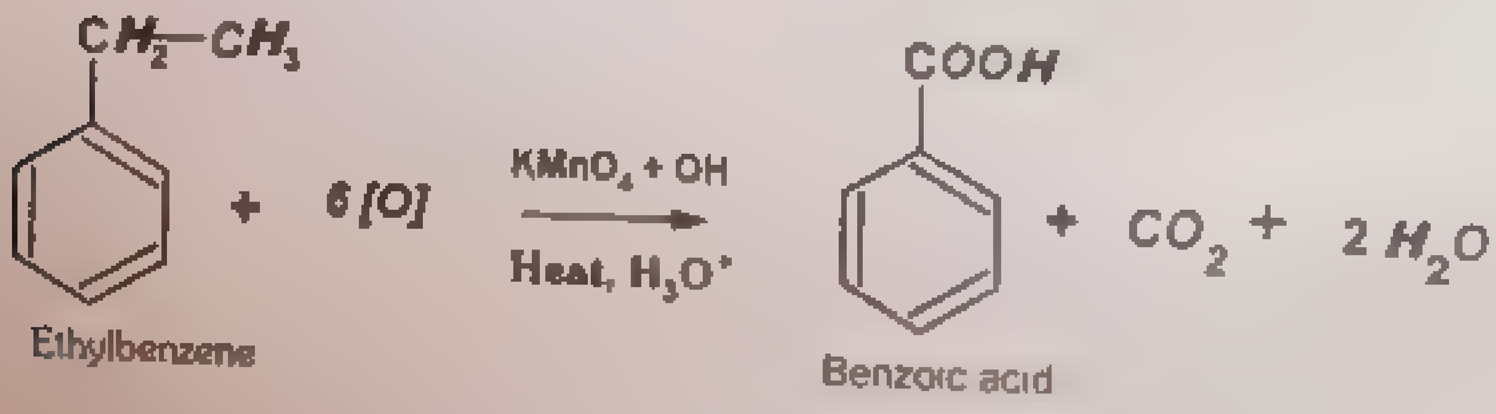


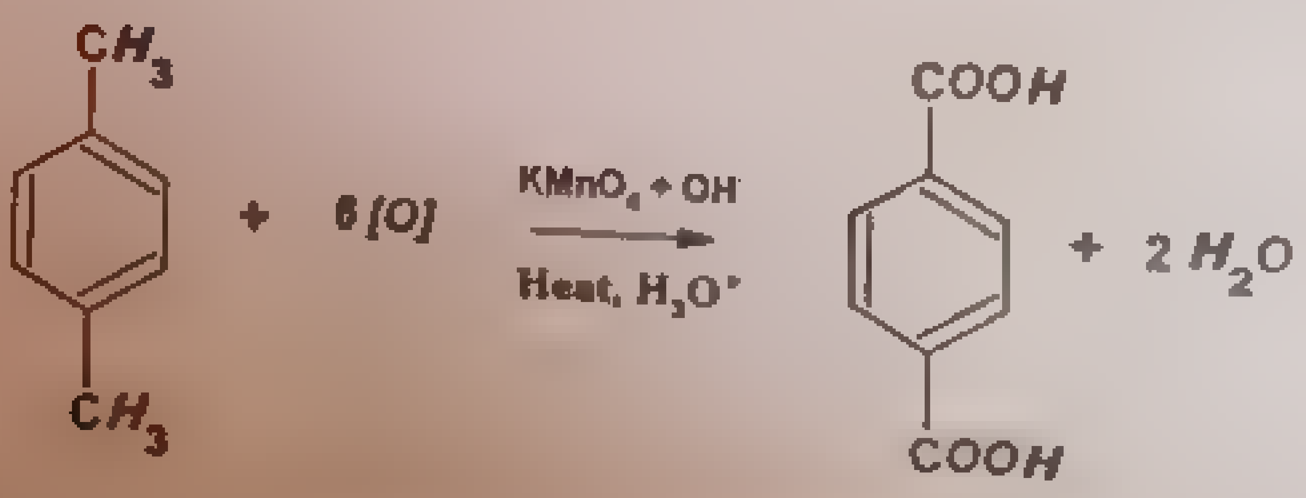
(4) OXIDATION OF SIDE CHAIN

Alkyl groups present in the benzene ring are oxidized into carboxylic groups. The oxidizing agents are

(i) $KMnO_4 + H_2SO_4$ (ii) $K_2Cr_2O_7 + H_2SO_4$ (iii) Dil. HNO







Conclusion:

When both methyl groups are oxidized and benzene ring remains unaffected [illegible] stable towards oxidizing agents

(C) – ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

General Introduction

The pi electrons of benzene are highly stabilized due to resonance. They are not readily [illegible] electrophilic attack like the electrons of alkenes. They [illegible] powerful electrophiles are required for a successful attack to penetrate and break the [illegible] cloud in benzene

Explanation and Example

Substitution of halogen in benzene requires iron or corresponding [illegible] molecule to produce a powerful electrophile

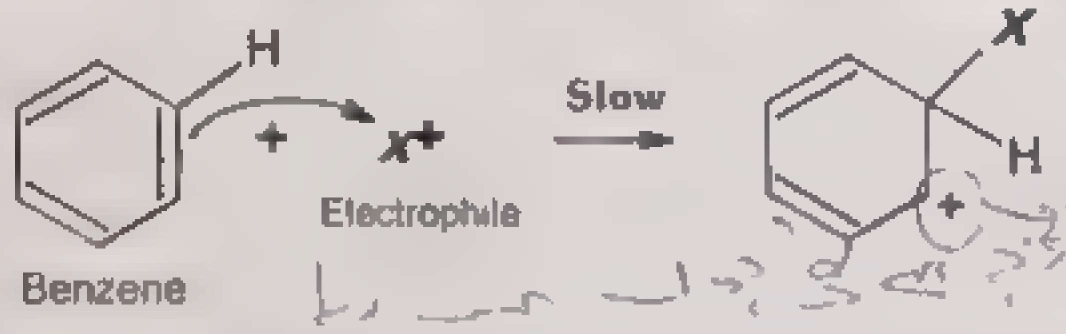
(i) Formation of a strong electrophile (X^+)

$$2Fe + 3X_2 \rightarrow 2FeX_3$$

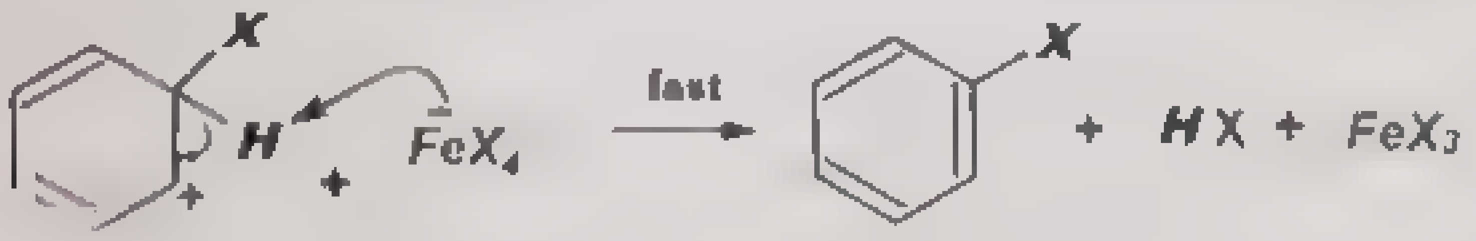
$$FeX_3 + X_2 \rightarrow \underset{\text{Tetra haloferrate ion (III)}}{FeX_4^-} + \underset{\text{Halogenoium ion}}{X^+}$$

(ii) Attack of electrophile at pi-bond:

- The halogenation ion thus produced attacks as a powerful electrophile on the electrons of [illegible]

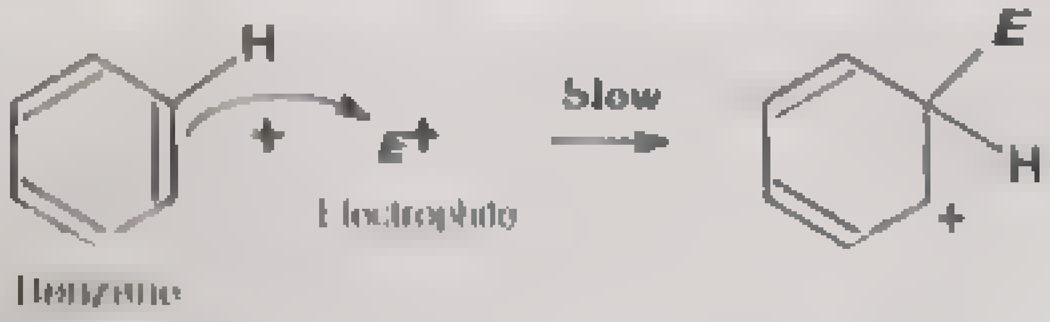


- It had benzene unstable. The stability is retained by the removal of H-atom to give substitution product



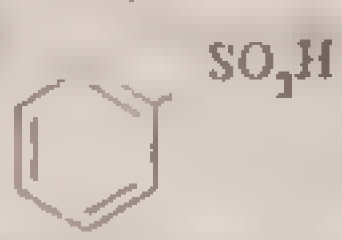
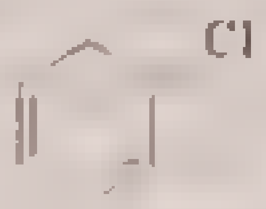
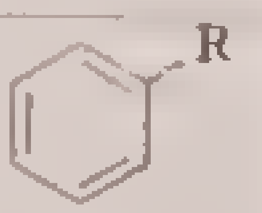
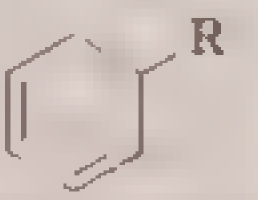
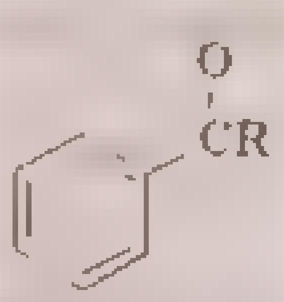
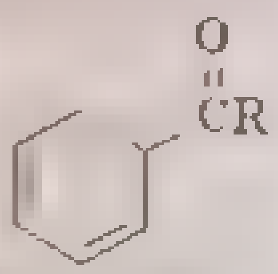
General Pattern of Substitution

The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows



Substitution is preferred over addition in order to pr[illegible]

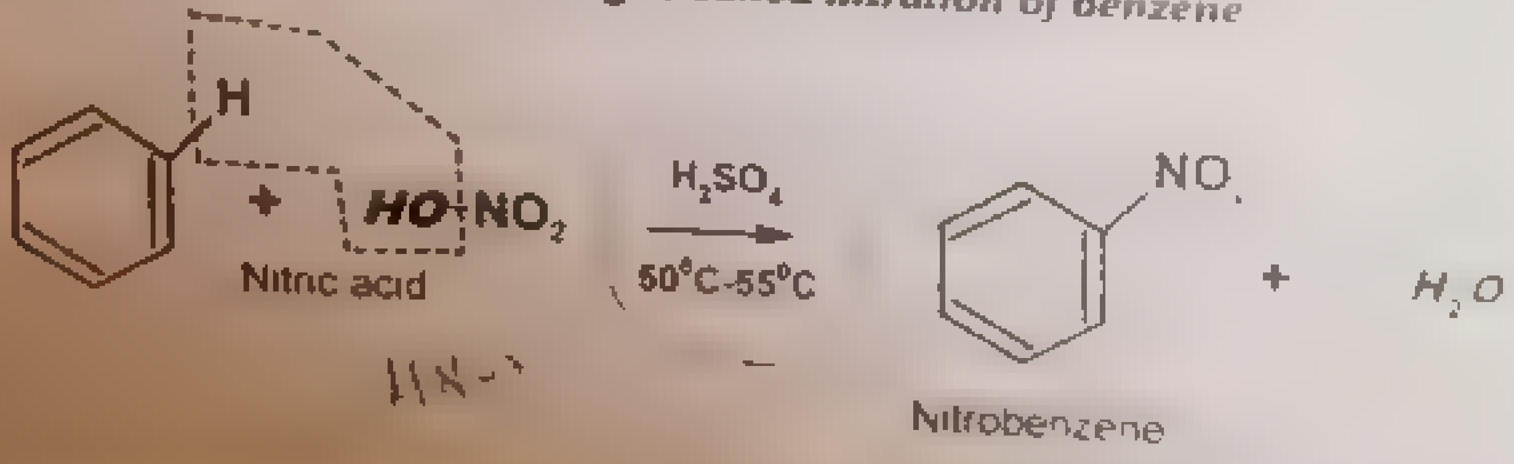
Summary

Reaction	Reagents	Electrophile	Product	Comments
Nitration	HNO_3 / H_2SO_4	NO_2^+		E^+ formed by loss of water fr...
Sulfonation	H_2SO_4 or SO_3 / H_2SO_4	SO_3		Reversible
Halogenation	Cl_2 / Fe or $FeCl_3$	Cl^+		E^+ formed by Lewis acid rea...
	Br_2 / Fe or $FeBr_3$	Br^+		E^+ formed by Lewis acid rea...
Alkylation	$RCl / AlCl_3$	R^+		E^+ formed by Lewis acid rea...
	ROH / H^+ (See Page 298 for carbocation generation)	R^+		E^+ formed by loss of water fro...
	$C=C / H^+$ (See Page 148 for ...)	R^+		[illegible]
Acylation	$RCOCl / AlCl_3$	RCO^+		[illegible]
	$RCO_2COR / AlCl_3$	RCO^+		[illegible]

Exercise Q3 (vi) ***Explain the following electrophilic substitution reactions of benzene with m...***
(b) Nitration

(1) NITRATION

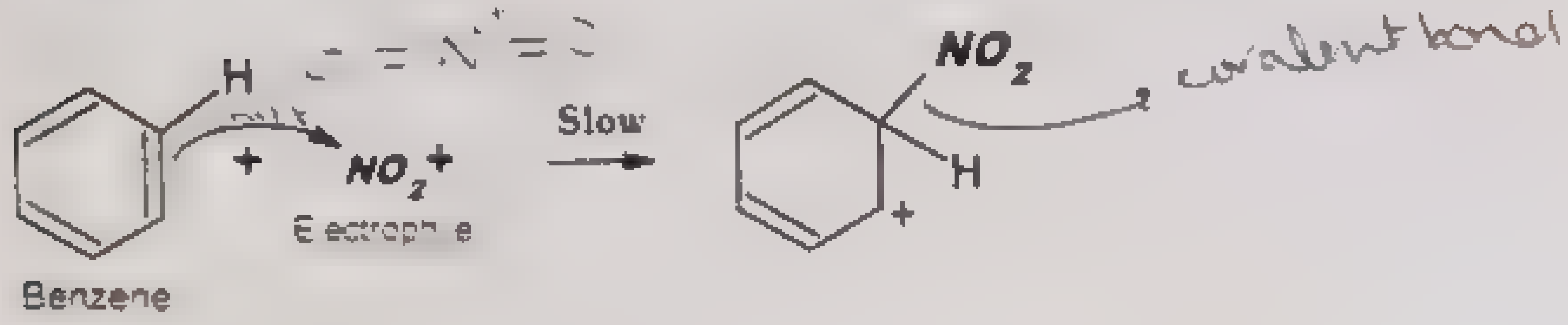
The introduction of nitro group in benzene ring is called nitration of benzene

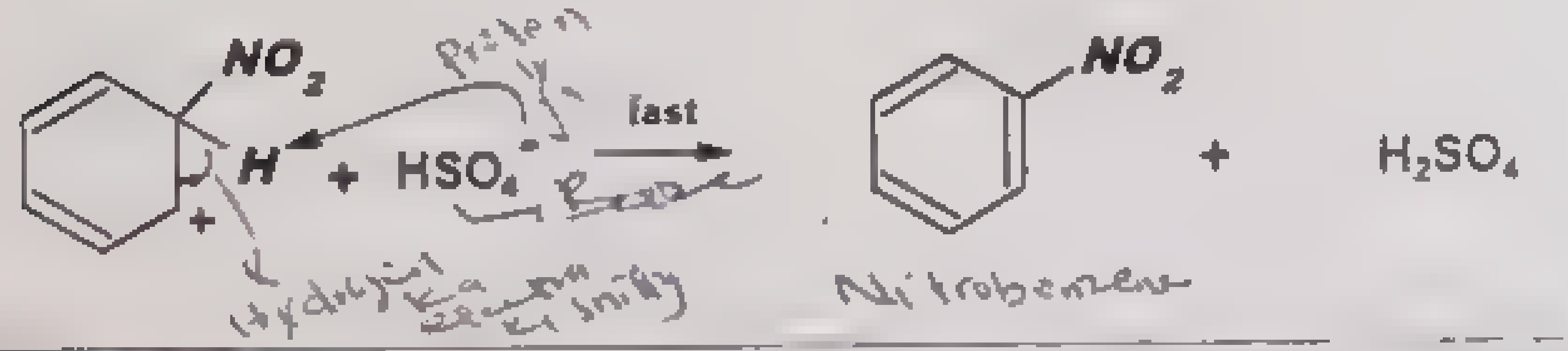


Mechanism

Sulphuric acid reacts with nitric acid to generate nitronium ion

$$HONO_2 + H_2SO_4 \xrightleftharpoons{50\,^\circ C} \overset{+}{N}O_2 + HS\bar{O}_4 + H_2O$$

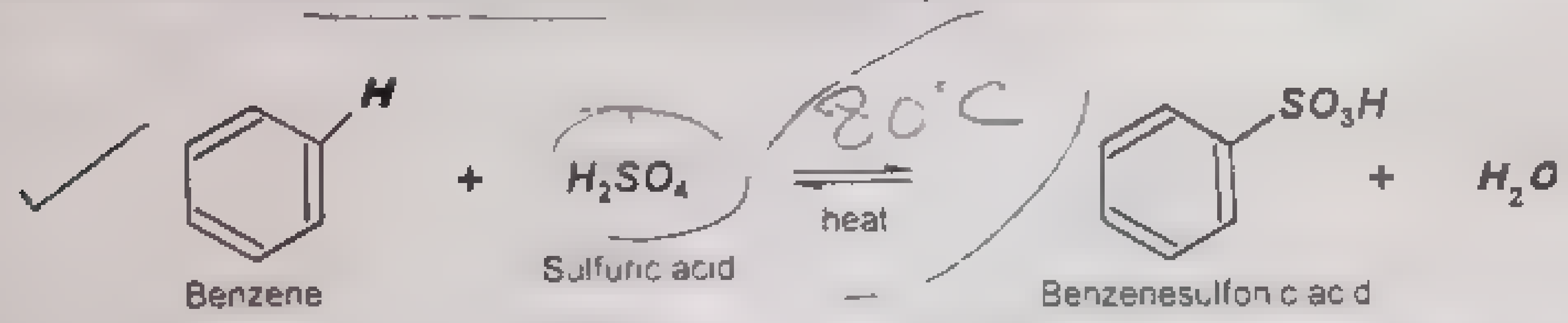




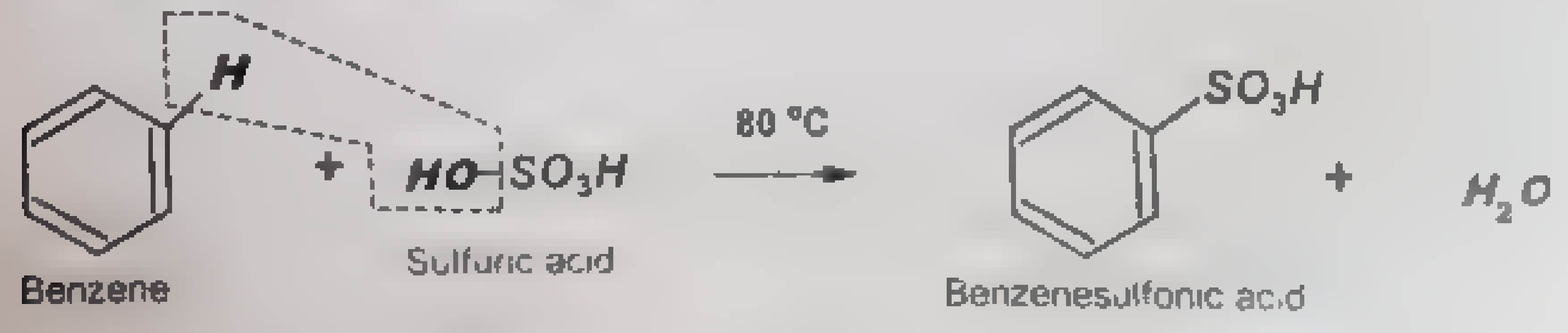
Exercise Q3 (vi) ***Explain the following electrophilic substitution reactions of benzene with mechanism.***
(c) Sulphonation.

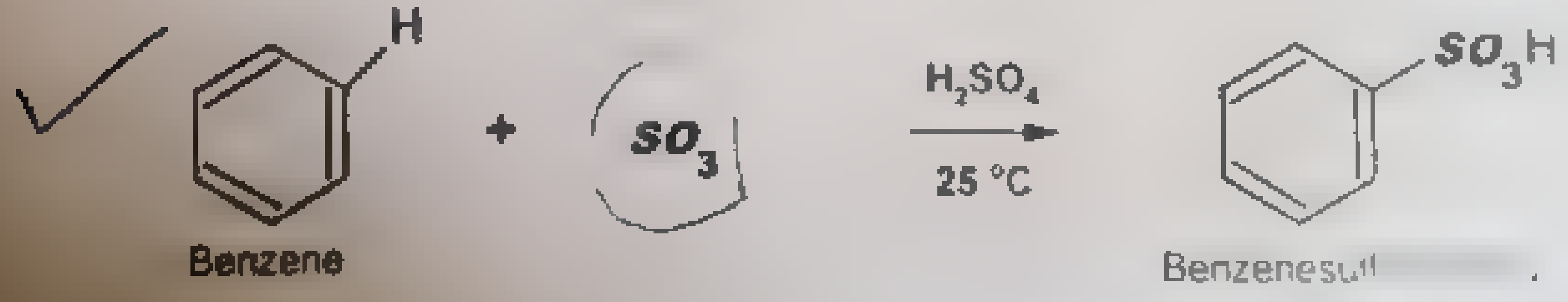
(2) SULFONATION

The introduction of sulphonic acid group in benzene rig is called Sulphonation



- When benzene is heated with fuming H_2SO_4 or concentrated H_2SO_4 it yields benzene sulphonic acid
- Fuming H_2SO_4 has free sulphur trioxide which is electron deficient (electrophile) and causes substitution

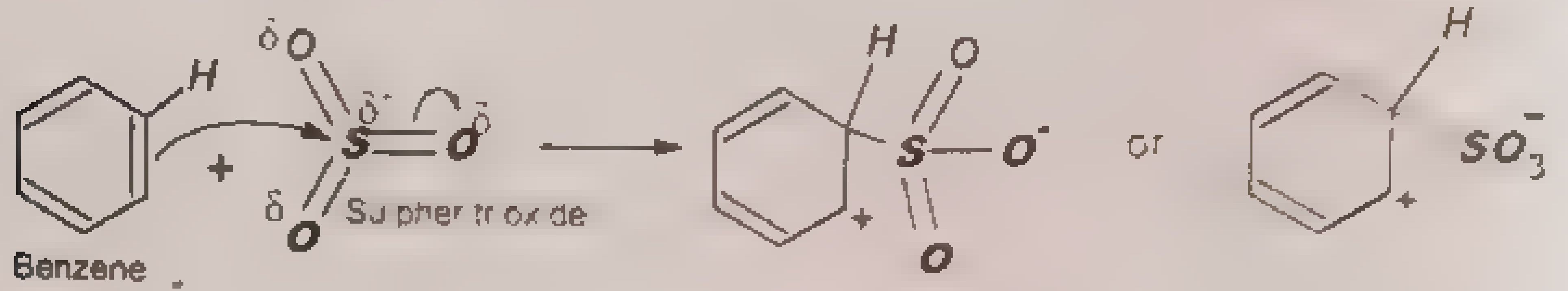


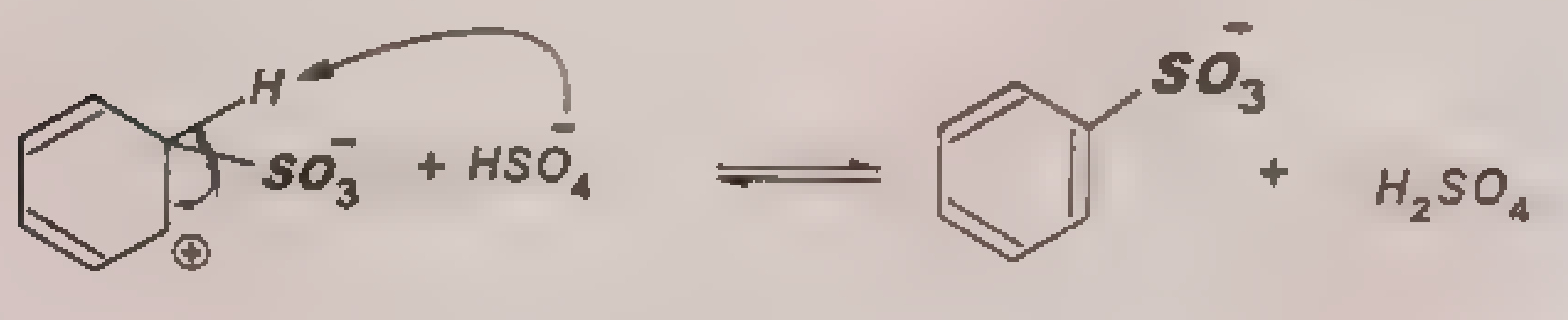


Mechanism:

When sulphuric acid alone is used, the actual elec...

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- + SO_3$$





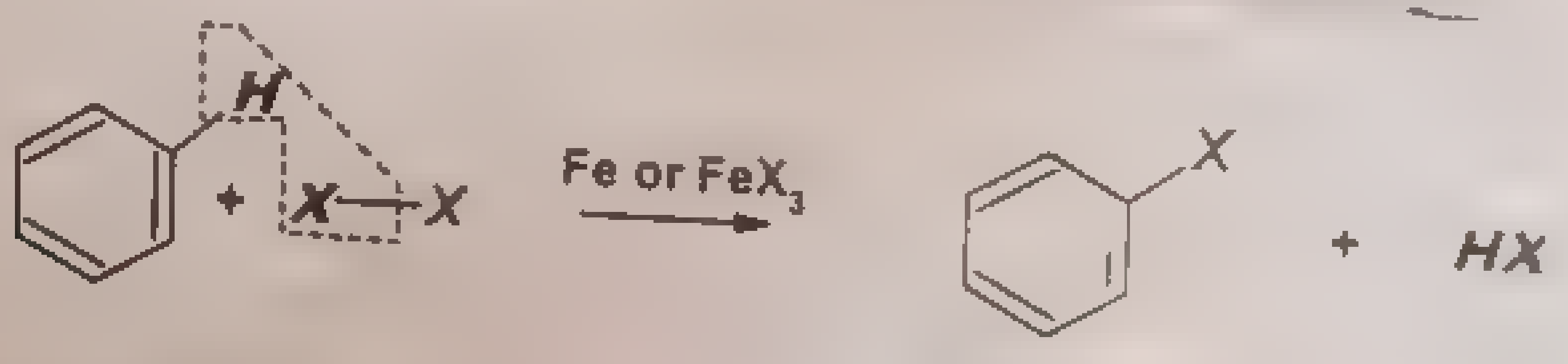
Exercise Q3 (6) Explain the following electrophilic substitution reactions of benzene with mechanism

(a) Halogenation

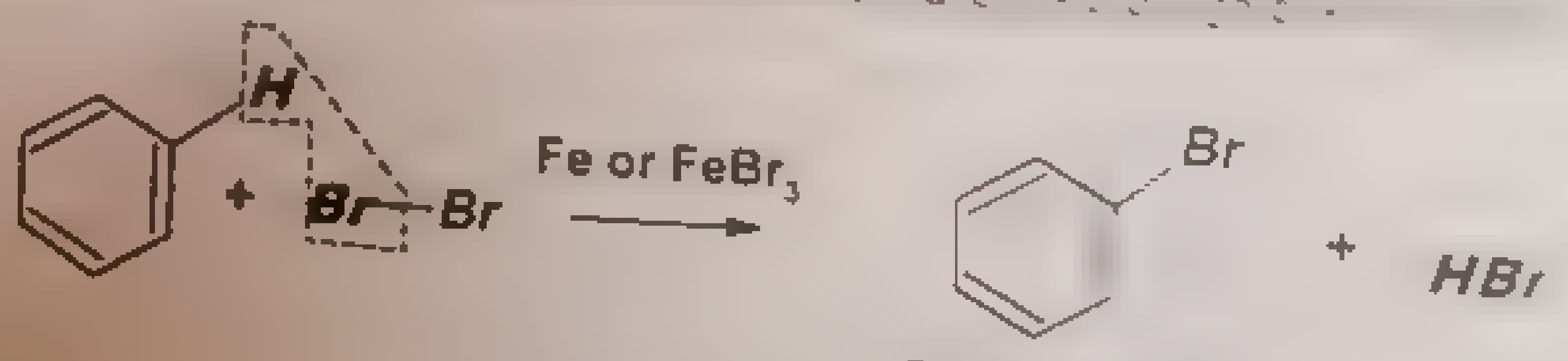
HALOGENATION

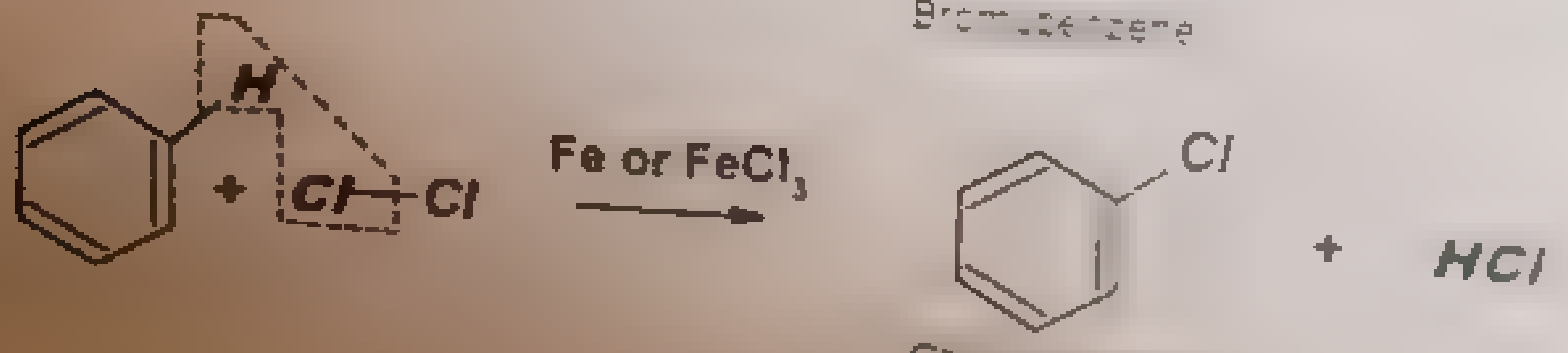
The introduction of halogen in benzene ring is called halogenation.

Halogenation of benzene occurs with halogens (X) in the presence of a catalyst FeX_3 or Fe



Chlorination and bromination are normal reaction but fluorination ... poor yield.





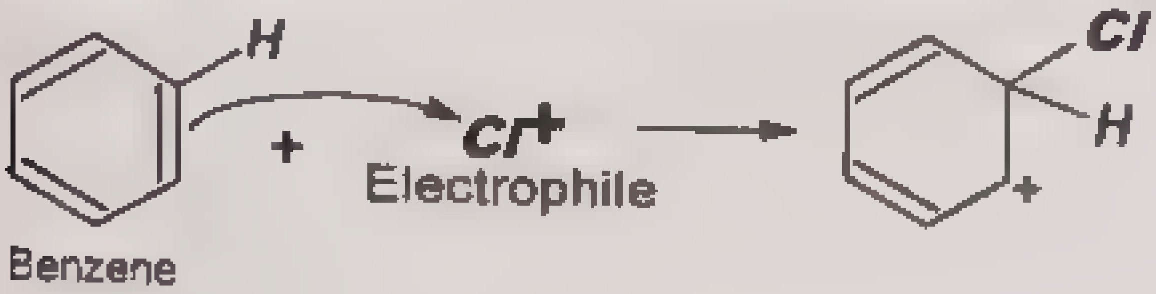
Mechanism:

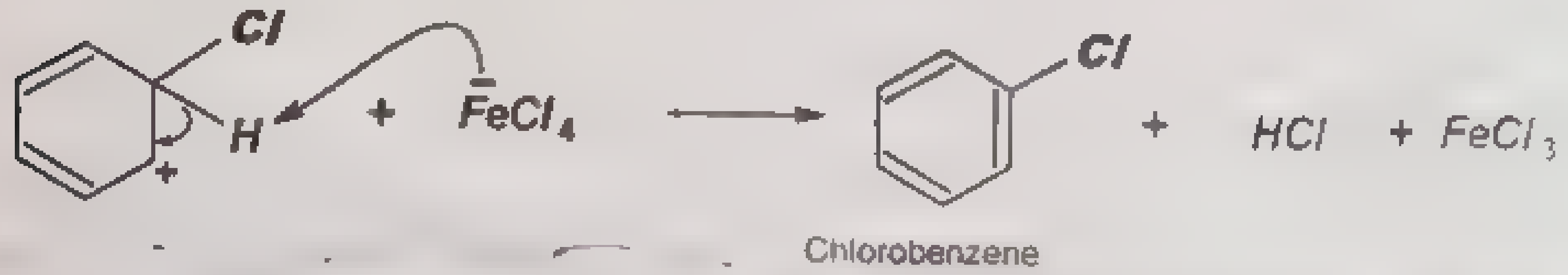
The actual halogenation agent is X^+ that is formed by the following mechanism

$$X_2 + FeX_3 \longrightarrow X^+ + \bar{F}eX_4$$

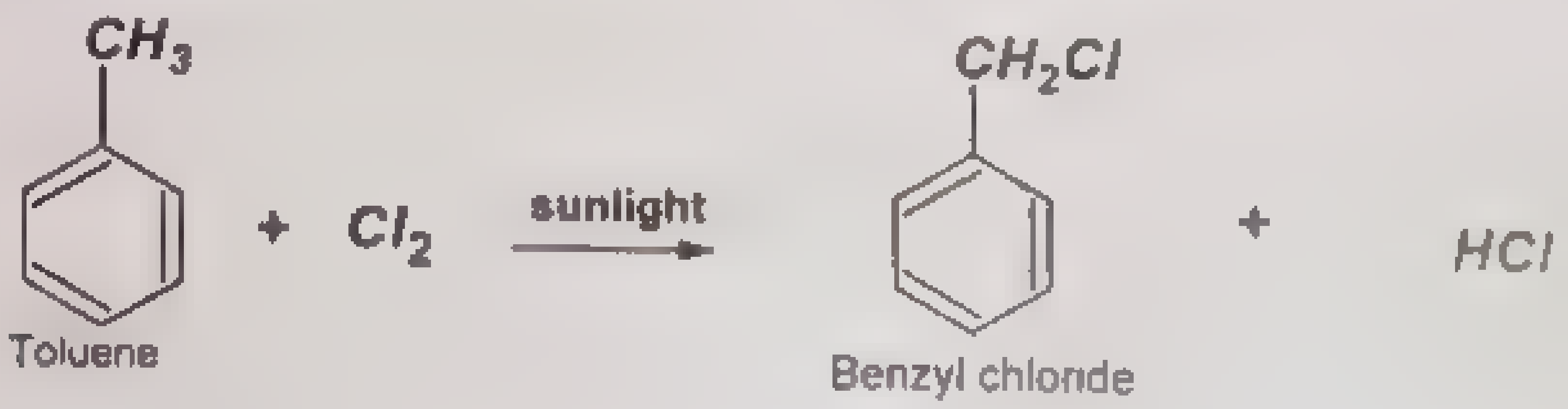
$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + \bar{F}eCl_4$$

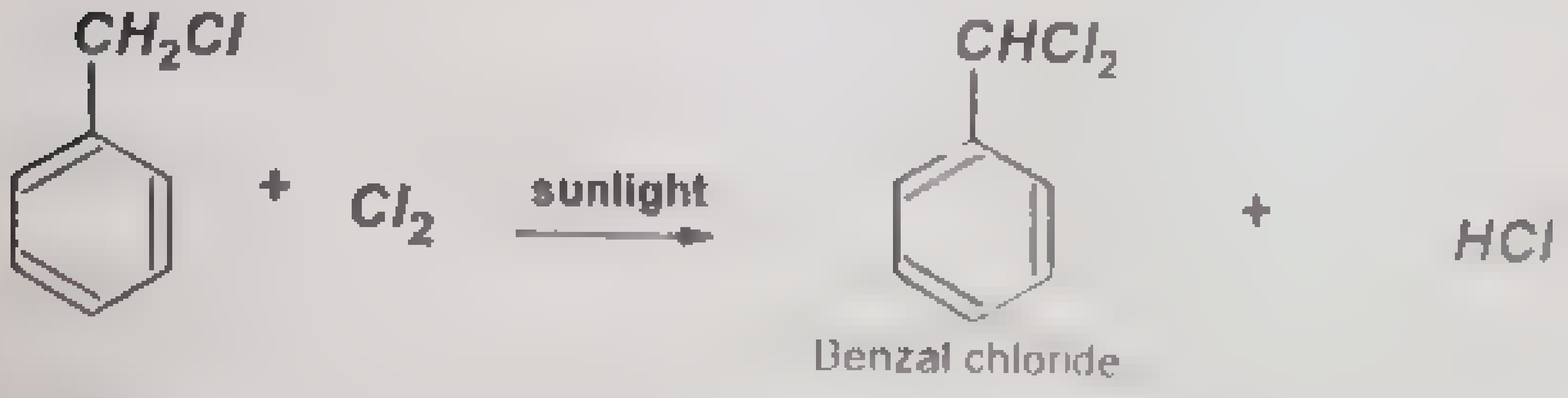
The Cl^+ being a strong electrophile is ready for successful attack on benzene

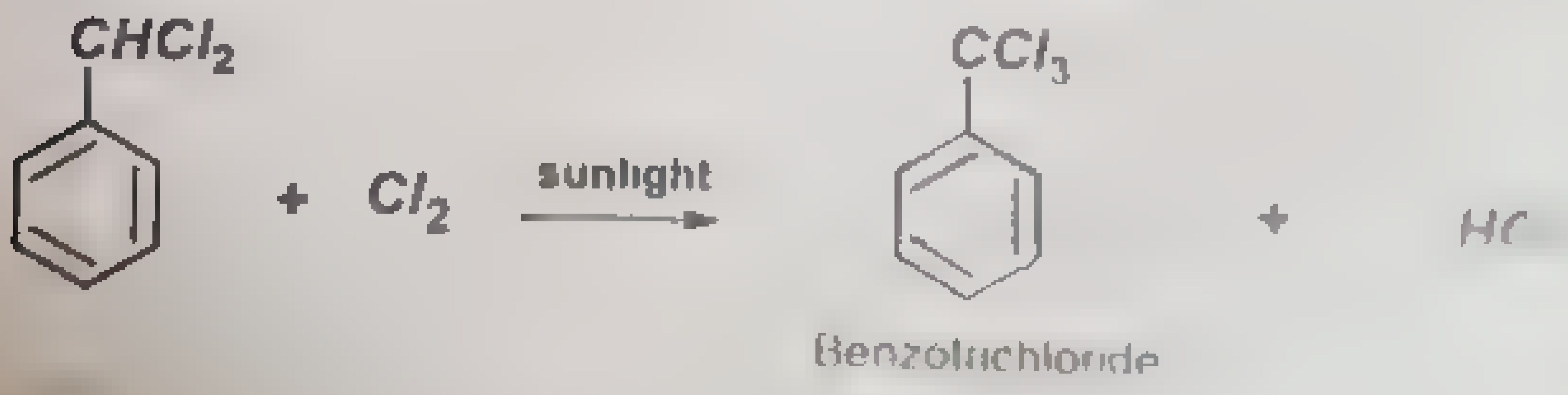




When alkyl benzenes are treated with chlorine or bromination the prese... are substituted

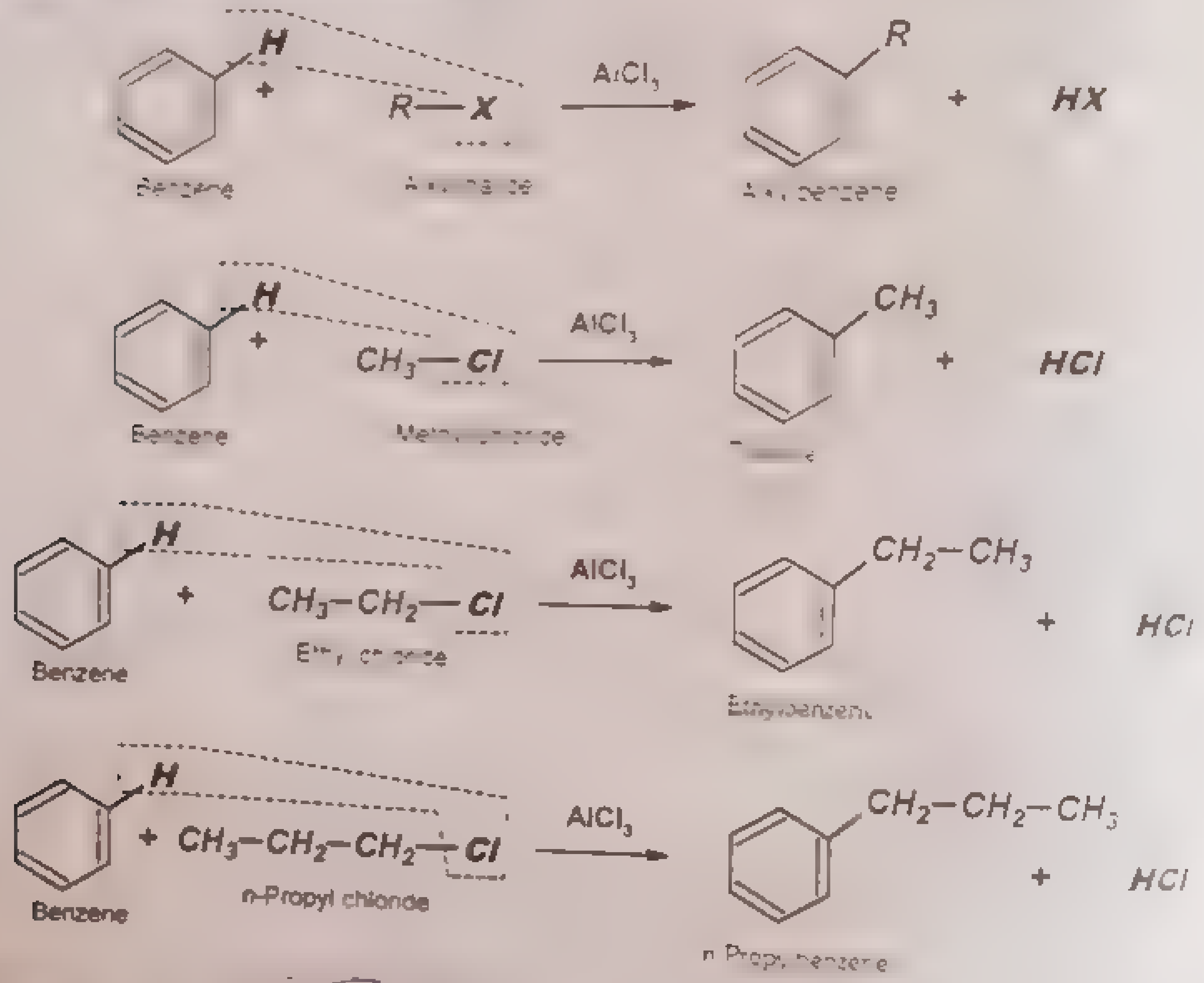




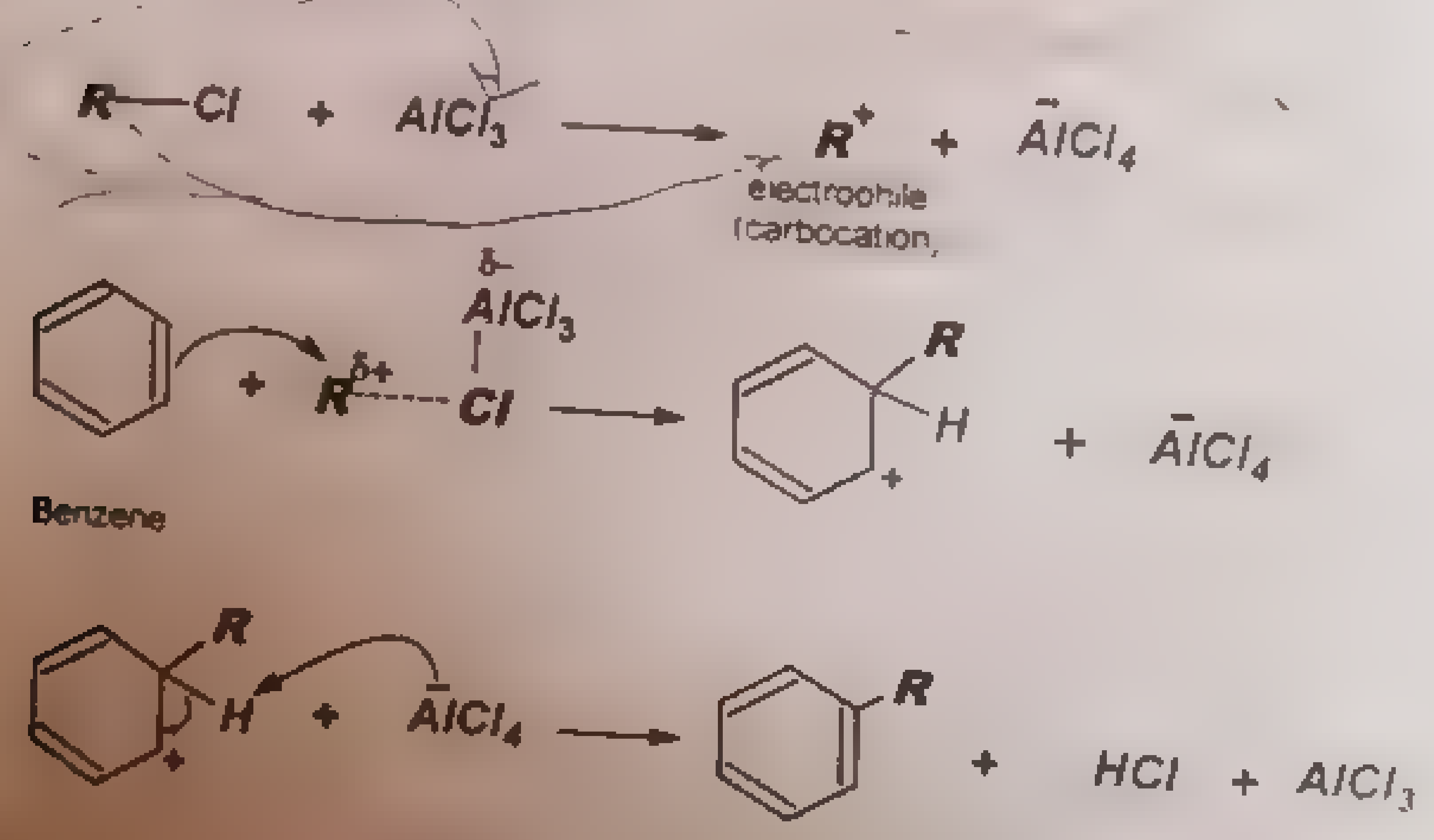


Exercise Q3.5 Explain Friedel Craft acylation and alkylation with complete mechanism

FRIEDEL-CRAFTS ALKYLATION

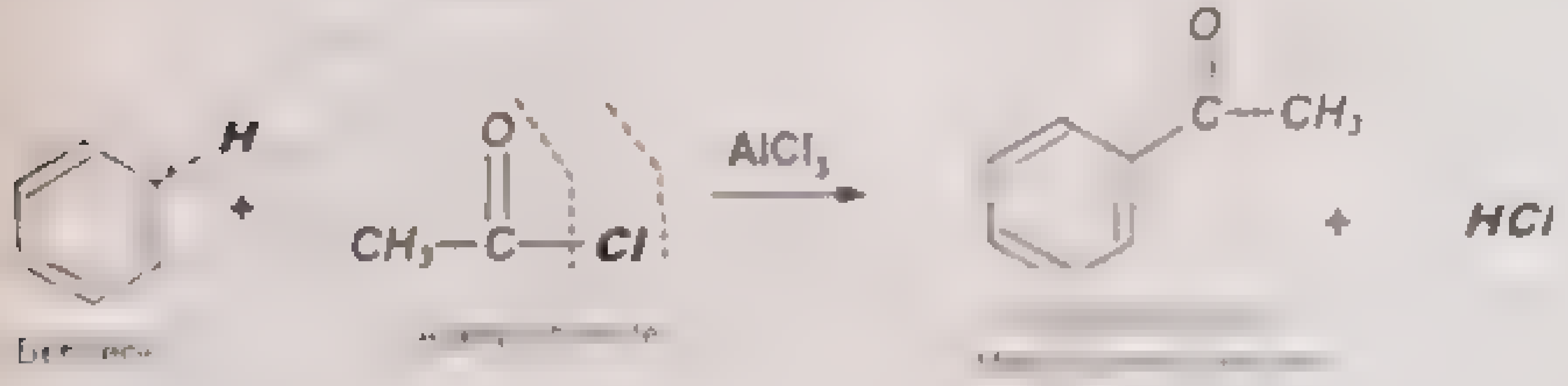


Mechanism:

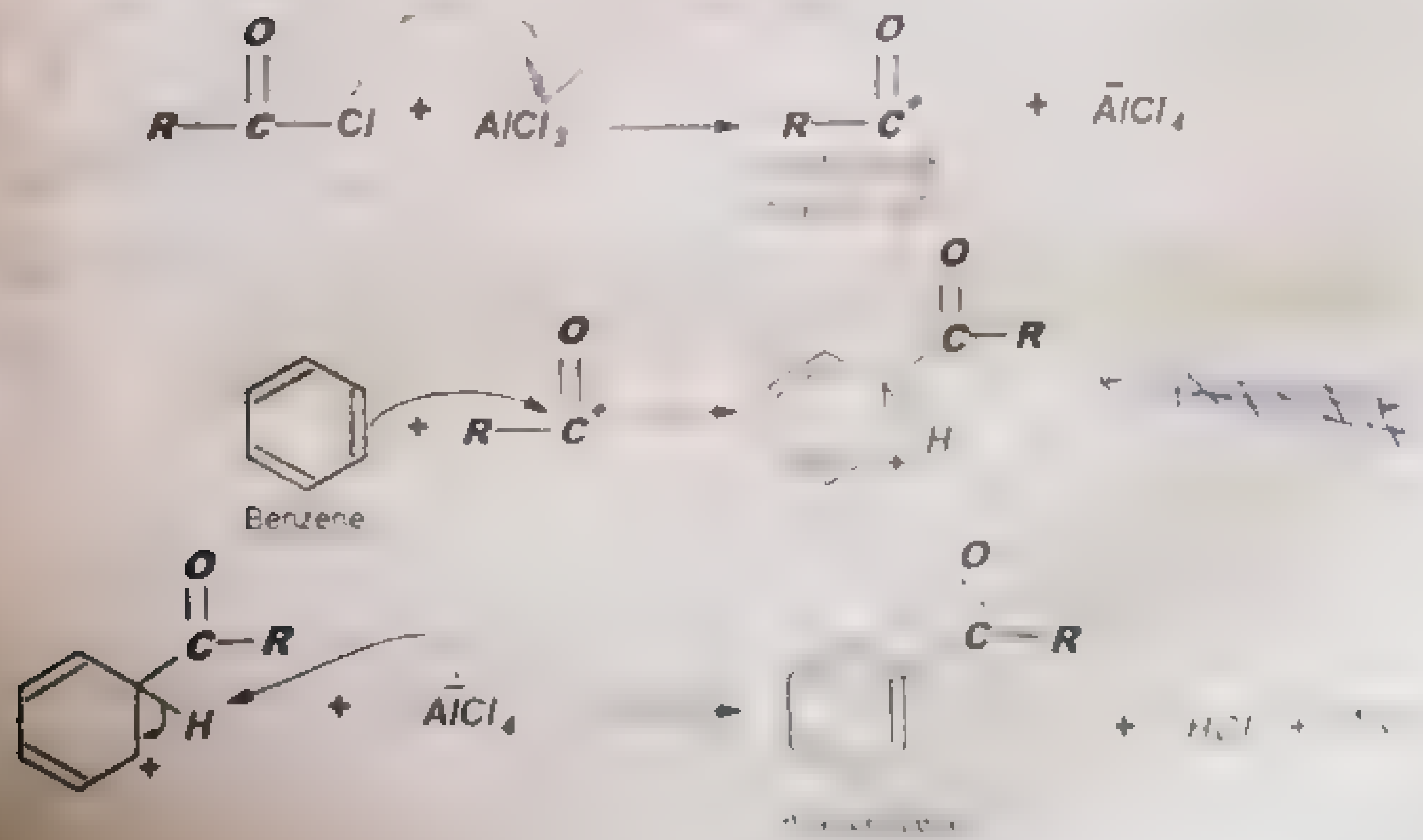


RIEDEL-CRAFTS ACYLATION

The introduc... R—C(=O)... [illegible]
...talyst $AlCl_3$ is called Friedel Crafts Acylation or Acylation



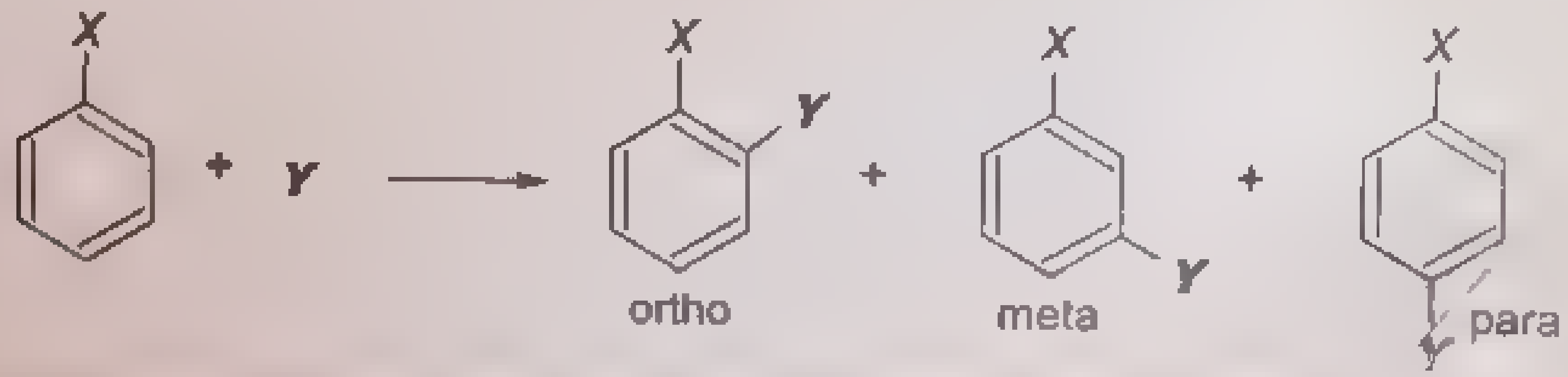
Mechanism



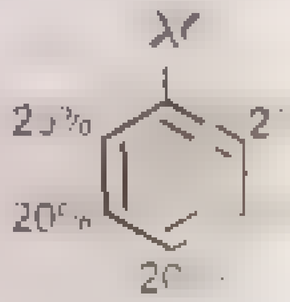
SUBSTITUENT EFFECTS

(Table of Substituent Effects) and Making Poly-substituted Benzenes

- When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent.
- However, the position of a second group into the ring depends on the nature of the first group. The substituted may enter in ortho, para or meta position.

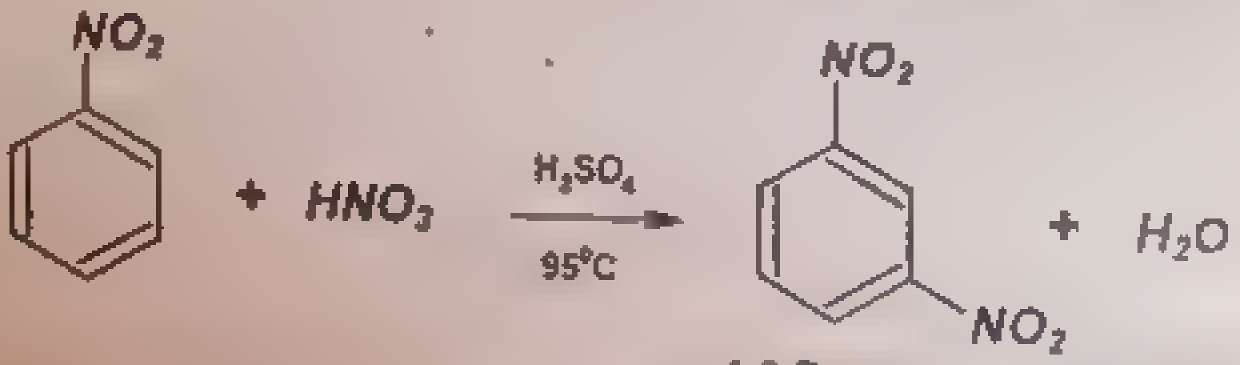


- On chance basis 40% ortho (20% + 20%), 40% meta (20% + 20%) and 20% para disubstituted products are expected.
- However, the results do not agree with chance substitution ratio



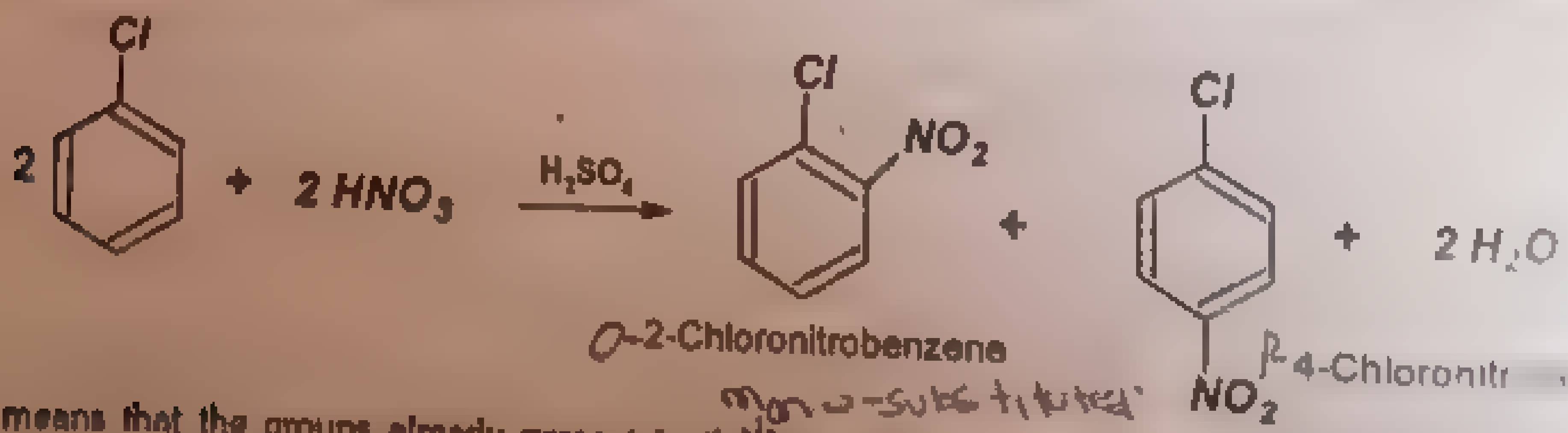
Examples

(i) m-nitrochlorobenzene is the main product of the following halogenation reaction



1,3-Dinitrobenzene

(ii) On the other hand, a mixture of 2 chloronitrobenzene and 4 chloronitrobenzene is obtained by nitration of chlorobenzene :



O-2-Chloronitrobenzene P-4-Chloronitrobenzene

mono-substituted

It means that the groups already present in the benzene ring directs the second incoming group and determines its position.

There are two types of groups

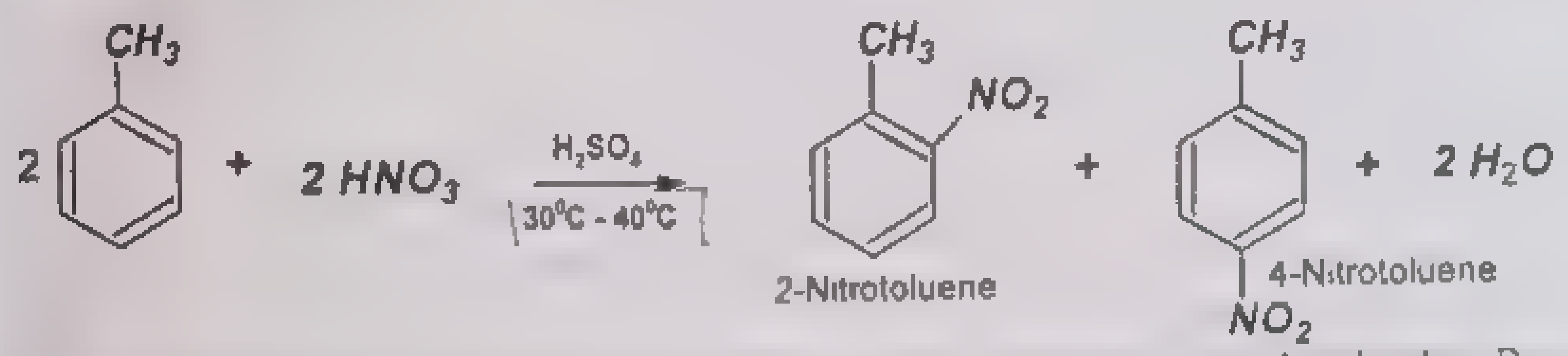
(1) ortho- and para-directing groups

(2) meta-directing groups

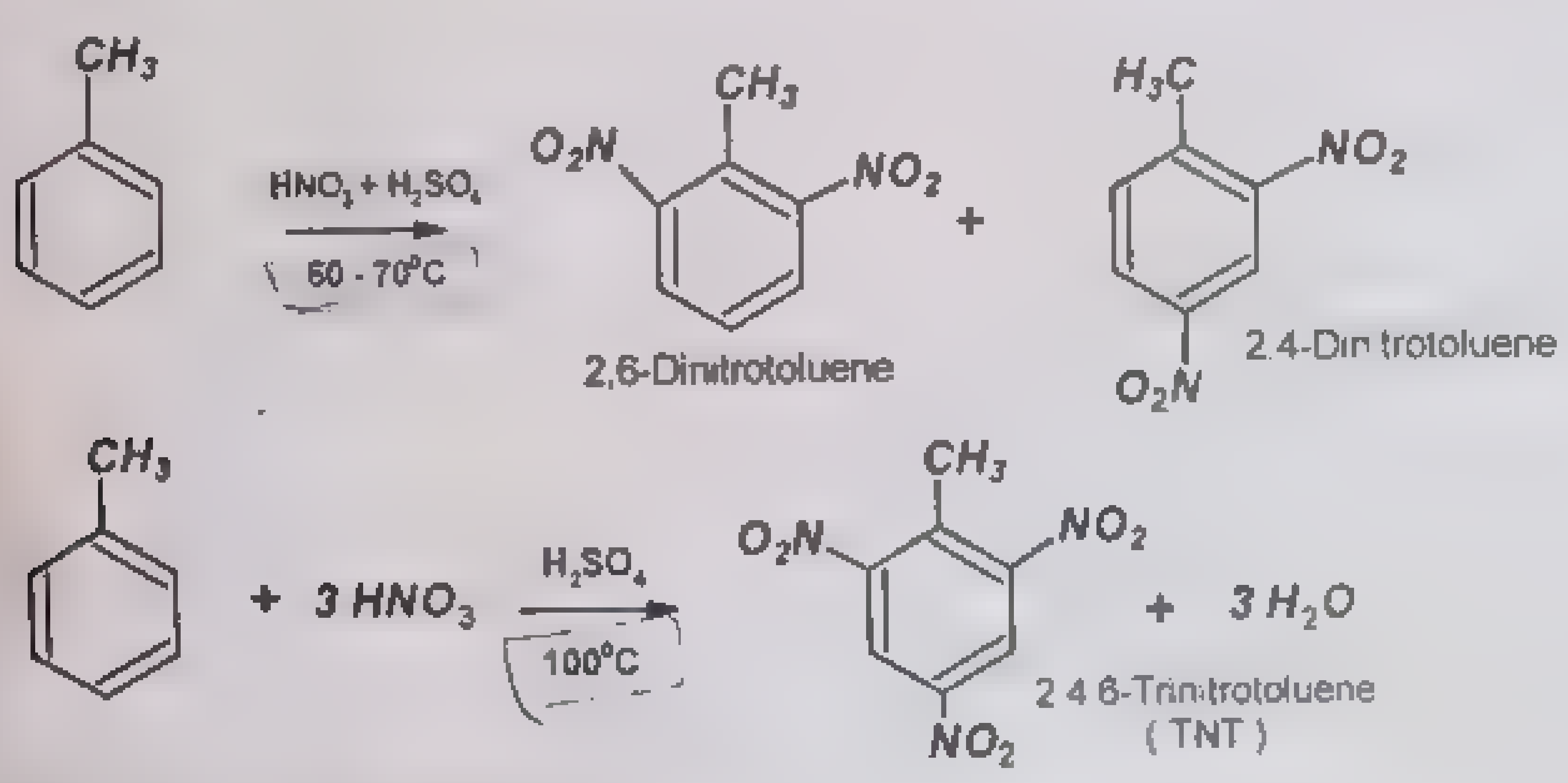
ORTHO AND PARA DIRECTING GROUPS

These groups release electrons towards the benzene ring, at *ortho* and *para* positions. Because these positions ... richer in electron for attack of an electrophile. The second group is substituted at ortho and para positions. They ...nerally increase the reactivity of benzene ring except halogens.

...ample:



The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this ...reased reactivity, more nitro groups can enter the ring.

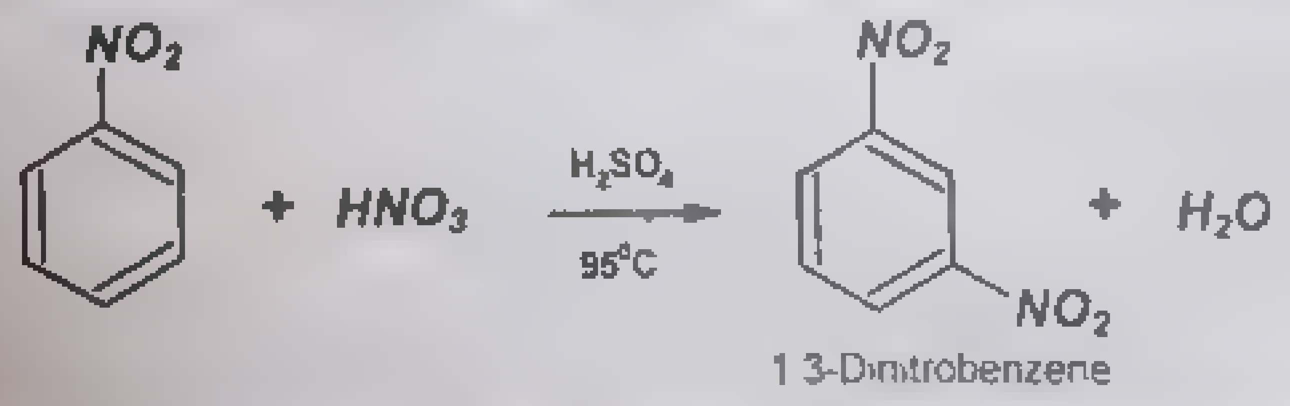


...amples (ortho- and para- directing groups)

$-N(CH_3)_2$, $-HNH_2$, $-OH$, $-OR$, $-OCH_3$, $-Cl$, $-Br$, $-I$

META-DIRECTING GROUPS

These groups withdraw the electrons of the benzene ring from ortho and para positions. Due to the electron ...hdrawing effect of such substituents, the ortho and para position are more electrons deficient than the meta ...sition. Thus the incoming electrophile will prefer to attack on meta position rather than ortho and para positions. ...ese groups are called meta-directing groups. These groups decrease the chemical reactivity of benzene.



The substitution of third nitro groups is not possible because nitro group has deactivated the ring.

...amples (meta-directing groups):

$-^{+}NR_3$, $-CN$, $-COOH$, $-CHO$, $-COR$

RULE:

If the electronegativity of the atom of the group attached to the benzene ring is greater than any atom ... group, the whole group will act as electron repelling/ will increase the reactivity of benzene ... entrant to ortho, para positions. On the other hand

If the electronegativity of such atom is less, it will be under constraint and it turn withdraw electron ... making it less reactive and directing the new entrant to meta position

Examples

(i) $-NH_2$ Nitrogen with greater electronegativity from hydrogen

(ii) $-Cl$ has no other atom hence will have no danger of pulling electrons. Thus it ... and p-directing group. Hence o- and p-directing

(iii) $-\overset{\overset{\large O}{||}}{N}-O$ Nitrogen with less electronegativity from O. Hence m-directing

(iv) In $-SO_3H$, the electronegativity of oxygen is greater than that of that of S hence oxygen ... which in turn withdraws electrons from benzene ring hence m-directing

MAKING POLYSUBSTITUTED BENZENES

Since the position of electrophilic attack on a substituted benzene ring is controlled by the substituent present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted be... need careful planning to ensure success.

The two factors that need to be monitored are:

- regiochemistry (region-selective means position on benzene ring)
- reactivity (for example Friedel-Crafts reactions are limited to halobenzenes and activated benzenes

QUICK QUIZ-7

1. (a) Describe the structure of benzene on the basis of following

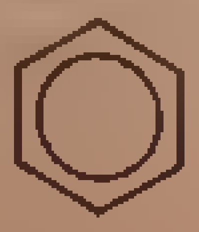
(i) atomic orbital treatment **Page 184**

(ii) resonance method **Page 186**

(b) Prove that benzene has a cyclic structure. (Exercise Q3 (4): will you prove that benzene has cyclic st...

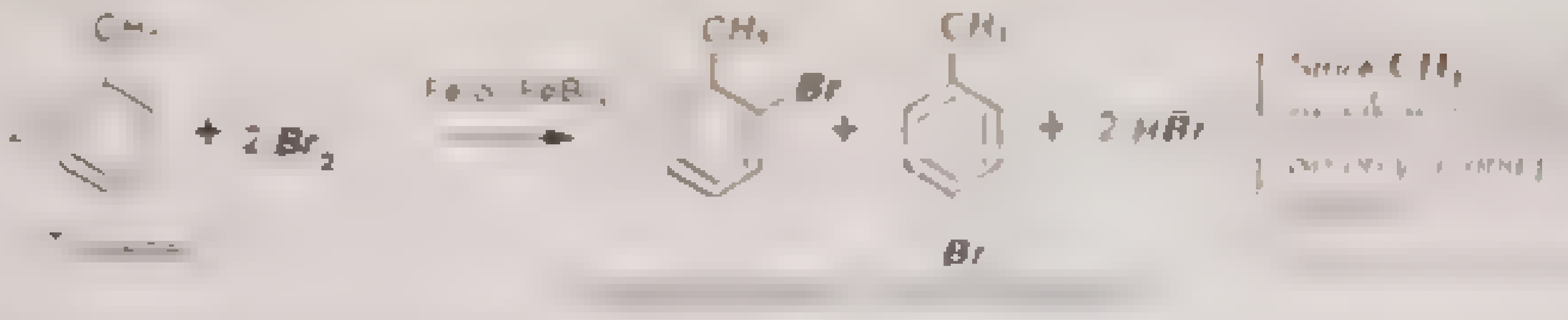
Benzene adds three hydrogen molecule which shows the presence of three double ... molecular formula of benzene is C_6H_6 which do not corresponds to any alkene or alkyne. He... should have cyclic structure. Moreover, the product formed during hydrogenation is cyclohex... cyclic compound.

The cyclic structure was given by KeKule and then confirmed by X-ray analysis ... benzene is



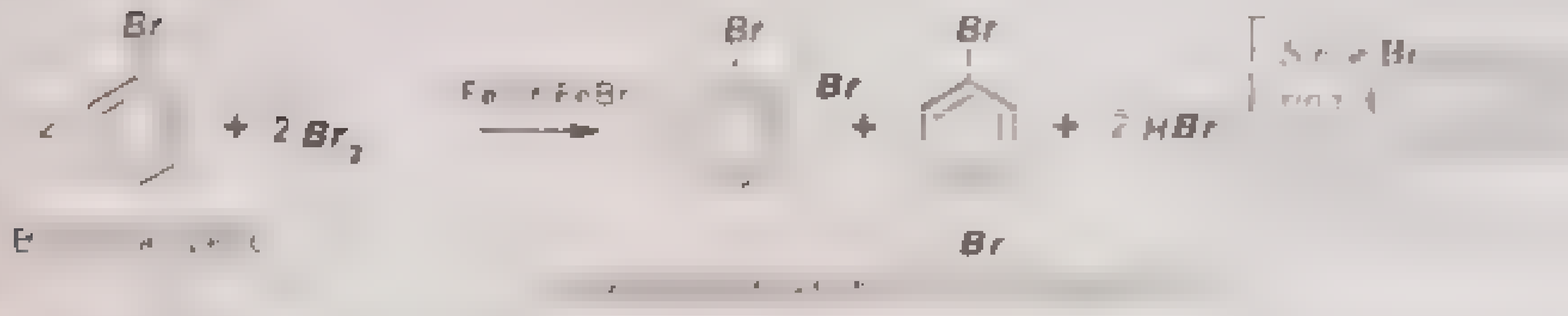
2. Predict the major products of bromination of the following compounds

a) Toluene

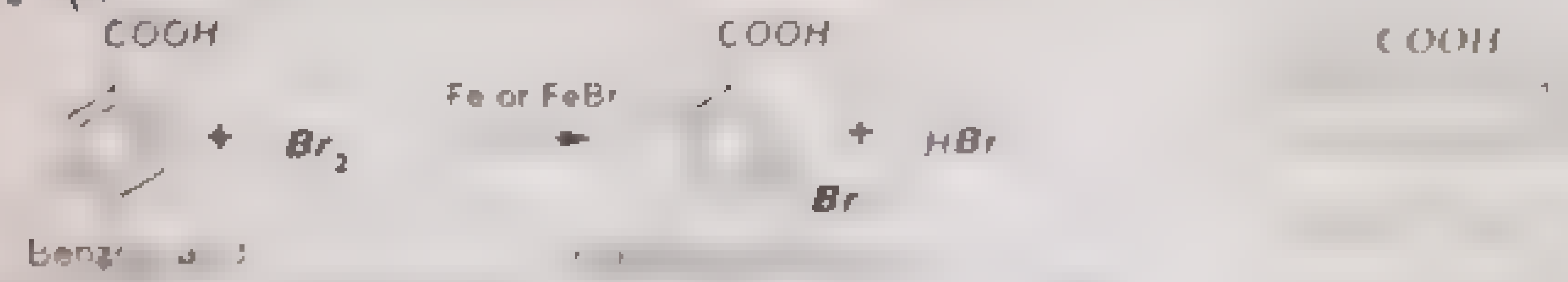


b) Nitrobenzene

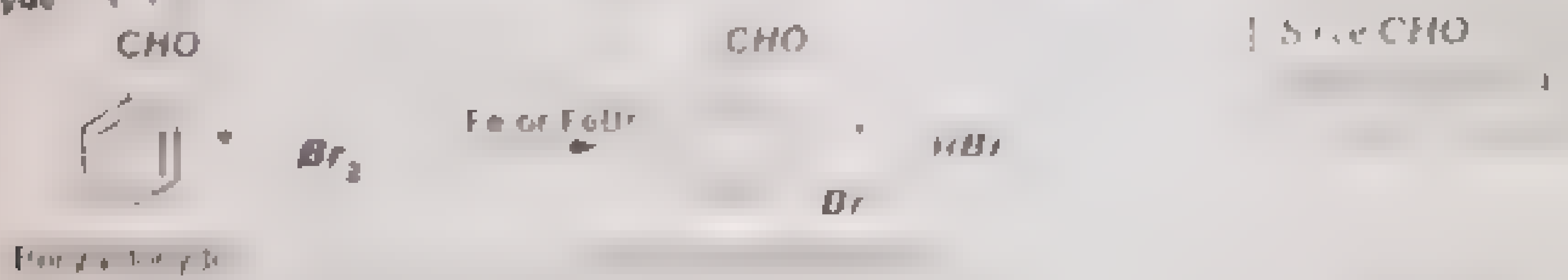
c) Bromobenzene



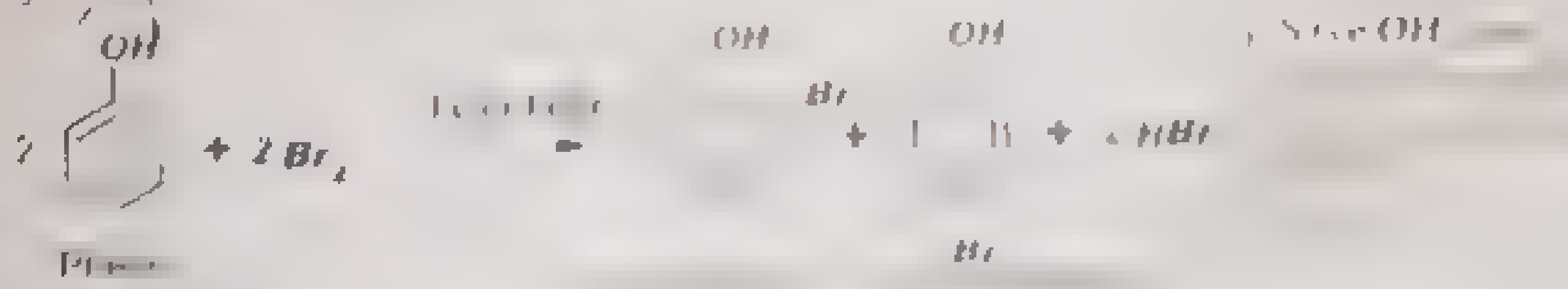
d) Benzoic acid



e) Benzaldehyde



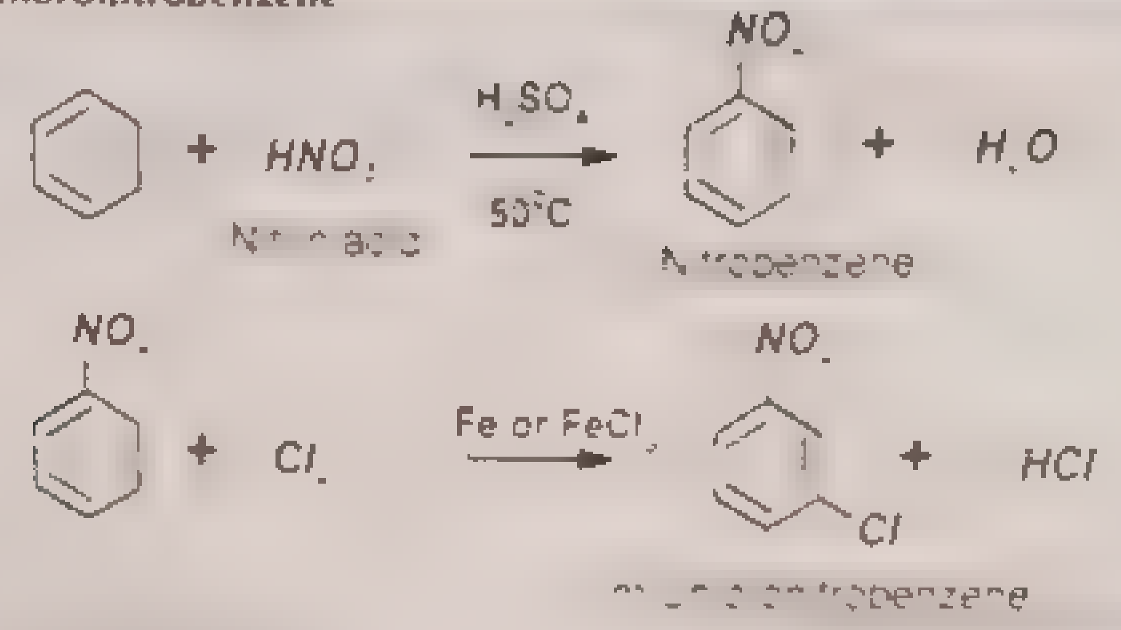
(f) Phenol



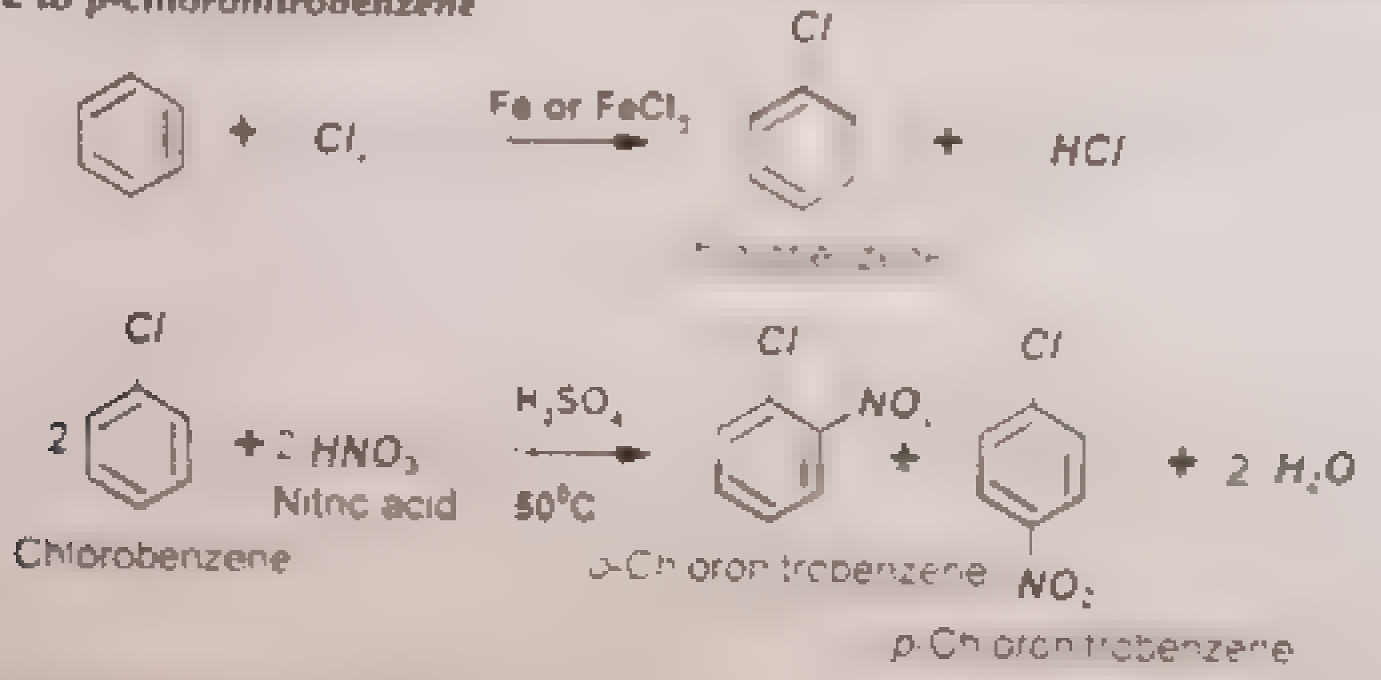
or

SOME IMPORTANT CONVERSIONS

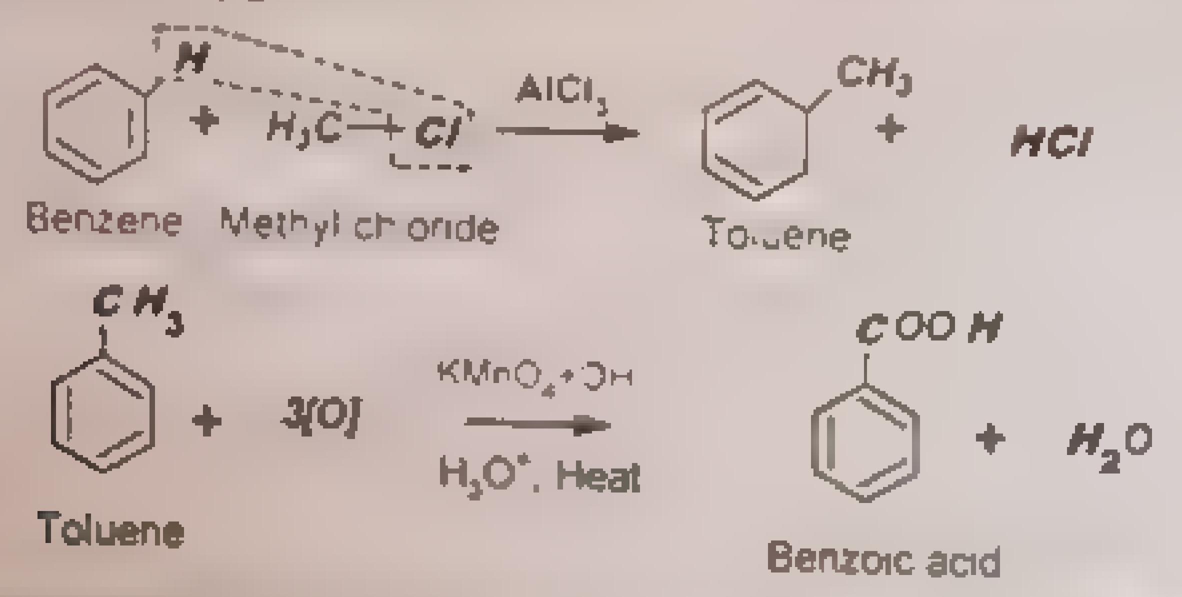
(i) Benzene to m-chloronitrobenzene



(ii) Benzene to p-chloronitrobenzene



(iii) Benzene to Benzoic acid



SOCIETY, TECHNOLOGY AND SCIENCE

HYDROCARBONS IMPORTANT AS FUEL FOR FUTURE ENERGY NEEDS OF PAKISTAN

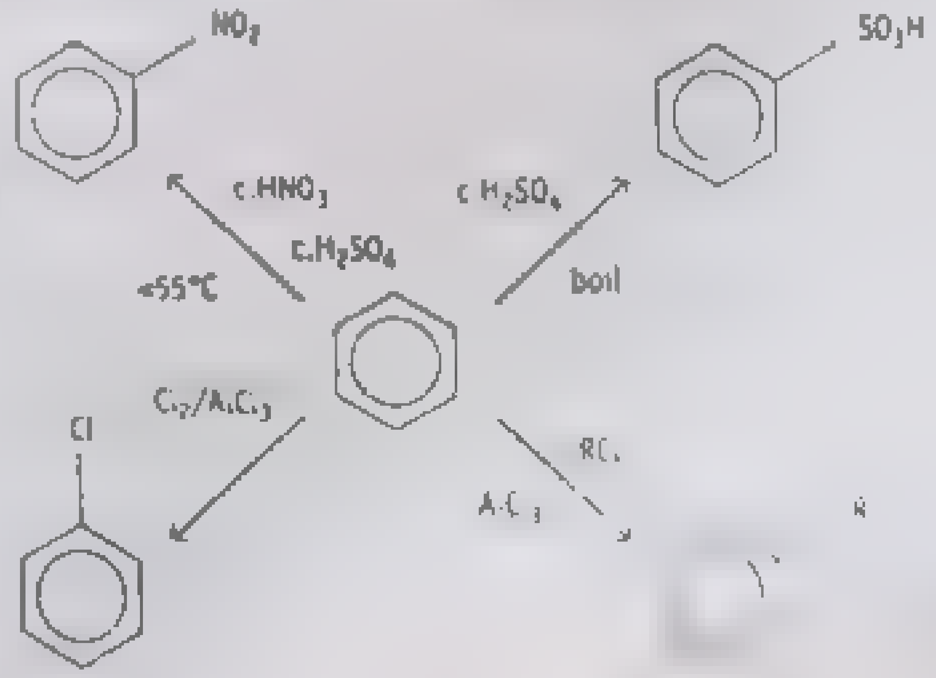
Ethanol, Natural Gas, Propane, Biodiesel - an alternative fuel based on vegetable oils or animal fats, Methanol also known as wood alcohol,P-Series fuels - a blend of ethanol natural gas liquids and methyl tetrahydro (MeTHF). P-Series fuels can be used alone or mixed with gasoline in any ratio by simply adding it to the

USES OF HYDROCARBONS

(1) Butane is used as a fuel in lighter
(2) Butane is also used in same camping stoves
(3) Crude petroleum is lighter than water.
(4) Coal is used for the manufacturing of synthetic petrol
(5) Ethylene is the hormone that causes tomatoes and apples to ripen
(6) Oxyacetylene torch is used for cutting of metals
(7) Methane is used to manufacture urea fertilizer
(8) Kekule was the scientist who draw the structure of benzene

KEY POINTS

- Compared to other functional groups alkanes tend to have low melting and boiling points and very low solubility in polar solvents such as water
- Alkanes are the simplest organic compounds, comprised of only sp^3 hybridized C and H atoms connected by s bonds They have a generic formula of C_nH_{2n+2}
- Branched alkanes are more stable than linear alkanes, e g 2-methylpropane is more stable than n-butane
- Alkanes react with halogens by a radical mechanism to give haloalkanes The mechanism consists of three steps, initiation propagation and termination
- Alkenes are unsaturated hydrocarbons with at least one C=C the double bond is composed of a δ and a π bond Carbon atoms in alkenes are sp2 hybridized
- Alkenes are very reactive compounds They undergo electrophilic reactions very easily
- Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's Rule
- Compounds that have the same molecular formula but different chemical structures are called *isomers*
  Constitutional (or structural) isomers differ in the order in which the atoms are connected so they contain different functional groups and / or bonding patterns
- *Example:* 1-propanol, 2-propanol and ethyl methyl ether (C_3H_8O
  Stereoisomers contain the same functional groups and differ only in the arrangement of atoms in space
- **Conformational** isomers (or conformers or rotamers) are stereoisomers produced by rotation about sigma bonds typically rapidly interconnecting at room temperature
- **Configurational** isomers are stereoisomers that do not readily interconvert at room temperature and can (in principle at least) be separated
- **Geometric** isomers are configurational isomers that differ in the spatial position around a bond with restricted rotation (e g a double bond
- **Optical** isomers are configurational isomers that differ in the 3D relationship of the substituents about one or more atoms
- **Enantiomers** are optical isomers that are non-superimposable mirror images
- **Diastereomers** are optical isomers that are not enantiomers
- Hydrocarbons containing a triple bond are known as alkynes or acetylenes
- Alkynes undergo addition reactions and two molecules of a reagent are added to it
- The decreasing reactivity order of alkanes alkenes and alkynes are as follows: Alkenes > Alkynes > Alkanes
- Aromatic hydrocarbons include benzene and all those compounds that resemble benzene
- Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons
- Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
- The electrons in benzene are loosely held and the ring acts as a source of electrons. Hence benzene is readily attacked by electrophiles in the presence of a catalyst
- Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitution are the main reaction of benzene
- Resonance energy of benzene is 152kJ/mole
- Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures
- The C_6H_5- group is called phenyl
- The characteristic reaction type of benzene is electrophilic substitution. Some important substitution reacts are shows on the following diargram



- Groups like NH_2, NHR, -OR, -SH, -OCOR, -X, -OH etc which increase the electron density in the nucleus and facilitate further electrophilic substitutions are known as ortho and para directing groups.
- Groups like CN,-CHO, NH_3, NR_3, CCl_3 which hinder further substitution in the benzene nucleus are known as meta-directing groups.

EXERCISE

Q1: Select the right answer from the choices given with each question.

(i) ***The molecule of ethane posses which hybridization;***

(a) sp^3 (b) sp^2 (c) sp (d) sp^3d

(ii) ***The sp^2 hybrid orbitals are oriented in space at one angle:***

(a) 109.5^0 (b) 180^0 (c) 100^0 (d) 120^0

(iii) ***The geometry of acetylene is,*** SP

(a) angular (b) bent (c) trigonal (d) linear

(iv) ***Which reaction is used as test for the presence of alkene,***

(a) reaction of cold diluted alkaline $KMnO_4$ (b) Combustion

(c) Polymerization (d) Catalytic hydrogenation

(v) ***The general formula of alkane is,***

(a) C_nH_{2n+2} (b) C_nH_n (c) C_nH_{2n} (d) C_nH_{2n-2}

(vi) ***Soda lime is,***

(a) NaOH (b) KOH (c) Mixture of Na and Ca hydroxide (d) CaO and NaO...

(vii) ***The marsh gas is***

(a) Ethane (b) Methane (c) Propane (d) Butane

(viii) ***Acidic hydrogen is present in***

(a) Acetylene (b) Ethane (c) Benzene (d) Ethene

(ix) ***The benzene molecule contains***

(a) Three double bonds (b) Two double bonds (c) One double bond (d) None of these

(x) ***The electrophile in aromatic sulphonation is:***

(a) H_2SO_4 (b) HSO_4^- (c) SO_3 (d) SO_4^{2-}

(xi) ***The conversion of n-hexane into benzene by heating in the presence of Pt is called,***

(a) Isomerization (b) Aromatization (c) Dealkylation (d) Rearrangement

(xii) ***Catalyst used for Friedal Craft's reaction is:***

(a) HNO_3 (b) $AlCl_3$ (c) $BeCl_3$ (d) NaCl

(xiii) ***Benzene cannot undergo***

(a) Elimination (b) Substitution (c) Oxidation (d) Addition

(xiv) ***Shape of benzene molecule is***

(a) Pyramidal (b) Liner planar (c) Trigonal (d) Hexagonal planar

(xv) ***In which one of the following compounds the benzene ring are isolated;***

(a) Naphthalene (b) Anthracene (c) Phenanthrene (d) Diphenyl metha...

(xvi) ***Two compounds have the same composition and also have the same atoms attached to the same at... although with different orientations in space. These compounds are***

(a) identical (b) Position isomers (c) structural isomers (d) stereoisomers

(xvii) ***The isomers of a substance must have***

(a) same chemical properties (b) same molecular weight

(c) same structural formula (d) same functional groups

(xviii) ***Ethanol and dimethyl ether are best considered:***

(a) structural isomers (b) stereoisomers (c) enantiomers (d) diasteromers

(xix) ***Alkenes show geometrical isomers due to***

(a) asymmetry (b) rotation around a single bond

(c) resonance (d) restricted rotation around a double bond

(xx) ***Geometrical isomerism is shown by***

(a) lactic acid (b) maleic acid (c) 1-butene (d) 1,1-dichlor...

(xxi) *A molecule is said to be chiral* [illegible]

(xxii) *Which of the statements is false regarding chiral com*[illegible]

(a) [illegible]

(xxiii) *An optically active compound*

(b) whe[illegible]

(d) in solu[illegible]

(xxiv) *Plane polarized light is affected by* [illegible]

(xxv) *It is possible to distinguish between optical isomers*

[illegible]

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (a) sp^3

In ethane [illegible] carbon atoms are sp^3 hybridized because each of them [illegible]

(ii) Ans: (d) 120°

[illegible]

(iii) Ans: (d) linear

Both carbon atoms of acetylene are sp hybridized [illegible] molecule of [illegible]

H—C≡C—H

(iv) Ans: [illegible]

[illegible]

(v) Ans: (a) C_nH_{2n+2}

The alkanes are saturated compounds [illegible] formula is C_nH_{2n+2}, e.g., the formula of [illegible]

(vi) Ans: [illegible]

(vii) Ans: (b) Methane

Methane is found [illegible] called marsh gas

(viii) Ans: [illegible]

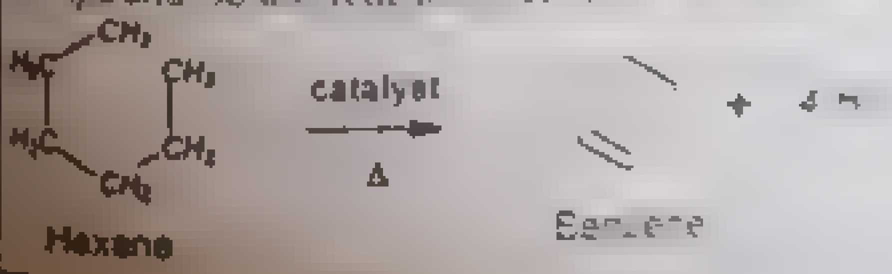
(ix) Ans: (d) None of these

In benzene mole[illegible] overlap with each other [illegible] p-electron cloud [illegible] are not present

(x) Ans: [illegible]

(xi) Ans: (b) Aromatization

Since an aromatic compo[illegible] compound, so this reaction [illegible]



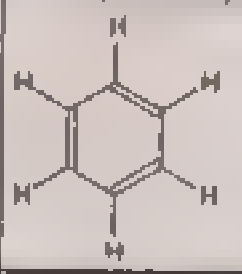
(xii) Ans: [illegible]

(xiii) Ans: (a) Elimination

Benzene give substitution, oxidation and addition reactions only. Elimination reactions are not possible

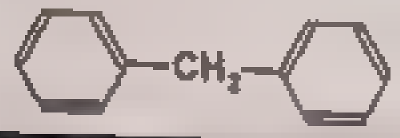
(xiv) Ans: (d) Hexagonal planar

X rays analysis ...



(xv) Ans: (d) Diphenyl methane

In Diphenyl methane, both benzene rings are isolated from each other



(xvi) Ans: (d) stereoisomers

By definition the compounds having ... atoms attached to the same atom ... orientations in space are stereo... called stereoisomerism

(xvii) Ans: (b) same molecular weight

The isomers have same molecular formula. Hence, they must have same molecular weight as well

(xviii) Ans: (a) structural isomers

Ethanol and dimethyl ether have same ... (C_2H_6O) but different ... group isomers of each other ... isomerism

CH_3-CH_2-OH Ethanol

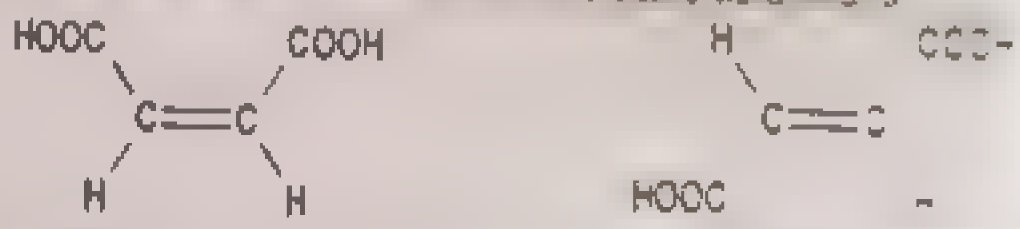
CH_3-O-CH_3 Dimethyl ether

(xix) Ans: (d) restricted rotation around a double bond

Free rotation cannot occur around double bond. So the rotation is restricted and geometrical isomerism is resulted

(xx) Ans: (b) maleic acid

Maleic acid ... the conditions of geometrical isomerism ... is a cis-isomer. Its other isomer is fumaric acid ...



Maleic acid (cis-isomer) Fumaric acid (trans-...)

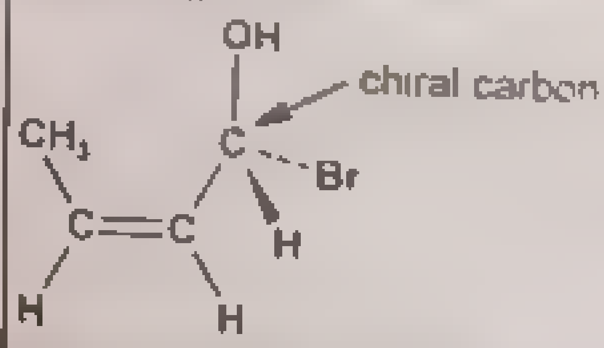
(xxi) Ans: (c) if it cannot be superimposed on its mirror image

By definition, a molecule which has non-superimposable mirror image is called a chiral molecule and it will show optical activity

(xxii) Ans: (b) have cis and trans isomers

cis- and trans-isomerism is ... related to the chiral nature of molecule ...

(NOTE: A chiral molecule ... if it fulfils the conditions of ... the following compound ... isomerism)



(xxiii) Ans: (b) when in solution rotate the plane of polarized light

An optically active compound must rotate the plane polarized light.

(xxiv) Ans: (c) chiral molecules

Chiral molecules are opt... rotate the plane polarized light

(xxv) Ans: (d) by polarimetry

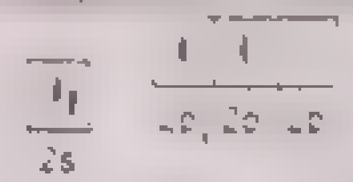
Optically isomers can rotate the plane polarized light in different directions. Thus they can be identified by polarimetry

Q2: Give brief answers for the following questions.

1. Why carbon is sp^3 hybridized in the compounds?

The valence shell electronic configuration of carbon is

$_6C$ **(ground state)**



SO, only two p-orbitals of C are partially filled therefore Carbon must form two bonds. However carbon is tetravalent in most of its compounds. Thus in excited state of carbon an electron from 2s orbital is promoted to an empty $2p_z$ orbital **i.e.,**

$_6C^*$ **(excited state)**

Thus C-atom becomes tetravalent. However since there is one s-orbital and three p-orbitals for bond formation therefore, valency is not equivalent. So, the four orbitals of C are mixed together to give four sp^3-hybrid orbitals which are used to form bonds with other elements in a tetrahedral geometry.

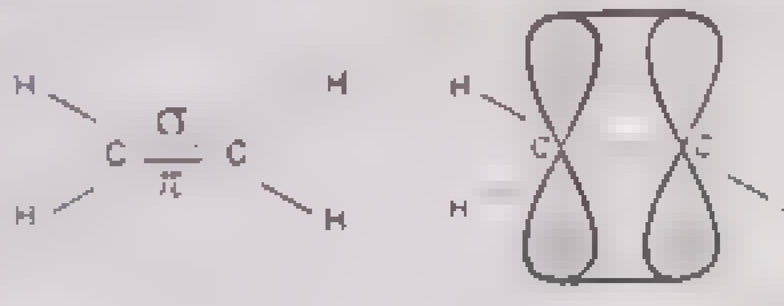
Hence, to explain the equivalent tetravalency and tetrahedral geometry of carbon atoms in compounds, idea of sp^3-hybridization is used

2. How is pi-bond formed in alkenes and alkynes?

Pi-bond formation in Alkenes

Consider the example of Ethene (C_2H_4)

- In C_2H_4, both carbon atoms show sp^2-hybridization
- The three sp^2-hybridized orbitals of each carbon atom are used to form C-C and C-H σ–bonds
- One unhybridized $2p_z$-orbital of two carbon atoms overlap sideways to form a π–bond

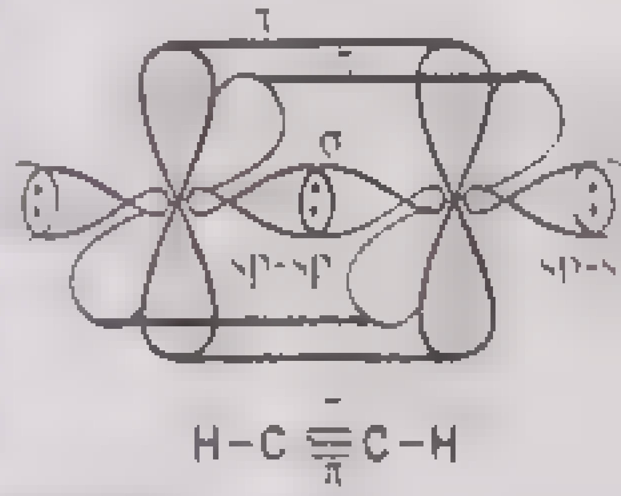


Pi-bond formation in Alkynes

2py

Consider the example of Ethyne (C_2H_2)

- In C_2H_2, both carbon atoms show sp-hybridization
- The two sp-hybridized orbitals of each carbon atom are used to form C-C and C-H σ–bonds
- The unhybridized $2p_y$ and $2p_z$ orbitals of two carbon atoms overlap sideways to form two π–bonds.



In π-bonds probability of finding electron is present above and below the internuclear axis.

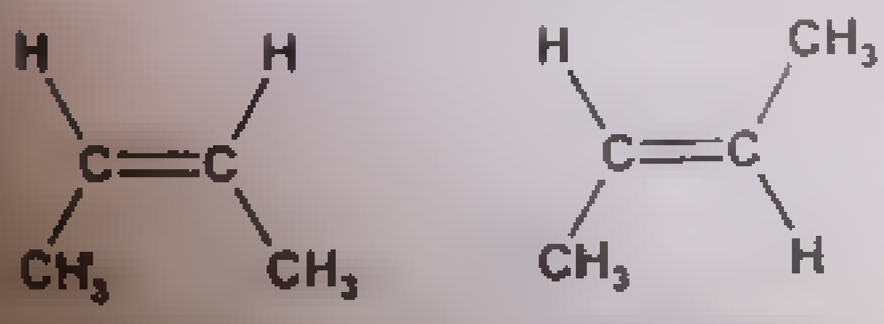
3. What is cis-trans isomerism?

Geometrical isomerism (also called cis trans isomerism) results from a restriction in rotation about double bonds or about single bonds in cyclic compounds

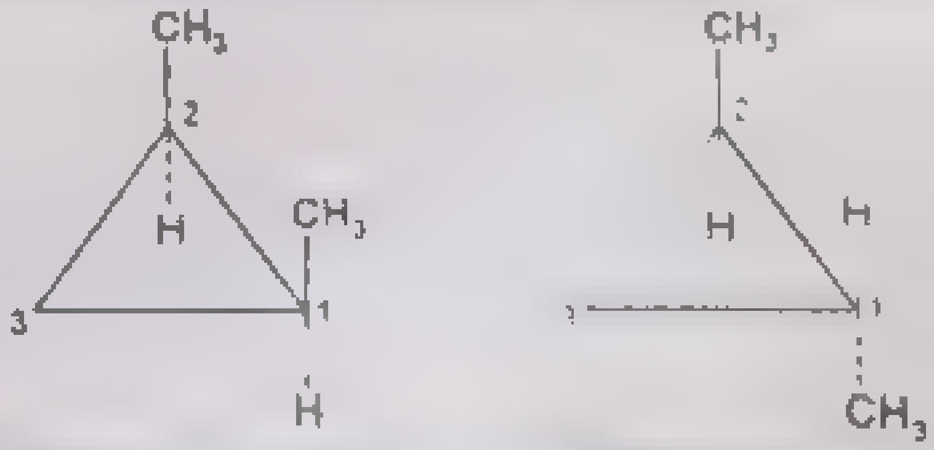
Conditions for cis-trans isomerism

- *Presence of double bond or cyclic ring*
- *Two different groups must be attached to each carbon of double bond, or to different carbons of ...*

Examples:



cis-2-Butene trans-2-Butene



4. Why alkanes are relatively chemically inert?

Alkanes are highly unreactive. Hence these are also called Parraffin (Latin, Parum = little, affins = affinity). Unreactivity of Alkanes is due to two factors

(i) Inertness of σ-bond

In a σ-bond the electrons are very tightly held between the nuclei. A lot of energy is required to brea... Moreover, the electrons present in a σ-bond cannot attack on any electrophile. Also no ... attack on them. Hence Alkanes less reactive.

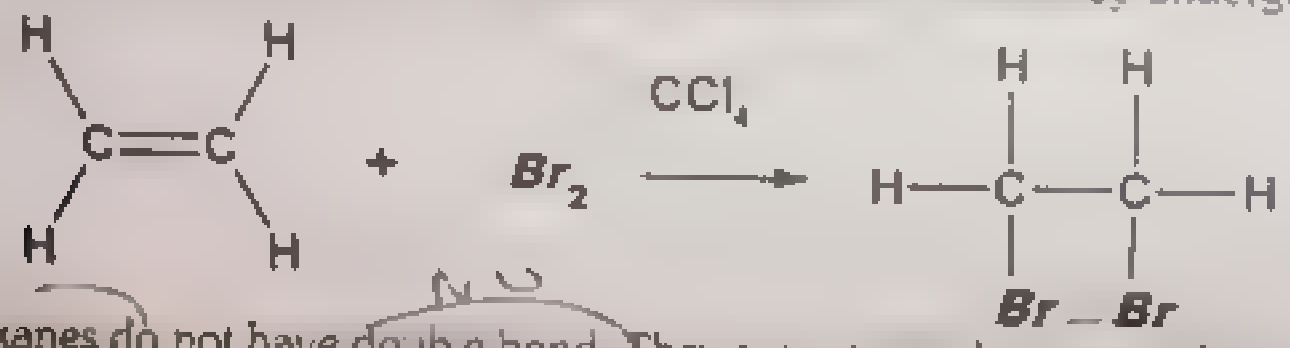
(ii) Non-polar Bonds:

The electronegativity of carbon (2.5) and hydrogen (2.1) do not differ appreciably. Therefore, the b... electrons between C-H and C-C are equally shared and bonds become non-polar. Hence, the ionic ... such as acids, alkalies, oxidizing agents etc. find no place in the alkane molecules for reaction.

Hence, alkanes are chemically inert.

5. Alkenes usually undergo addition reactions while alkanes do not why?

Alkenes are unsaturated and contain double bond. Thus they undergo electrophilic addition reaction. **e.g**



Alkanes do not have double bond. They are saturated compounds so they do not give addition reaction. Instead they give substitution reactions. **e.g.**

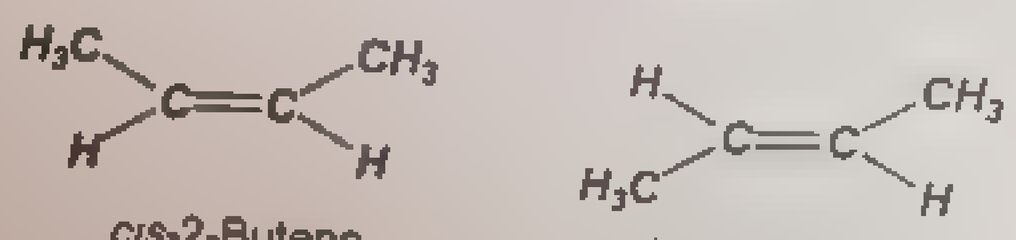
$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

6. What is stereoisomerism?

The isomers having equal number of same types of bonds, with identical connectivity, but diff... arrangement of atoms in space are called stereoisomers and the phenomenon is called stereoisomerism. The study of such isomers is called stereochemistry.

It is of two types

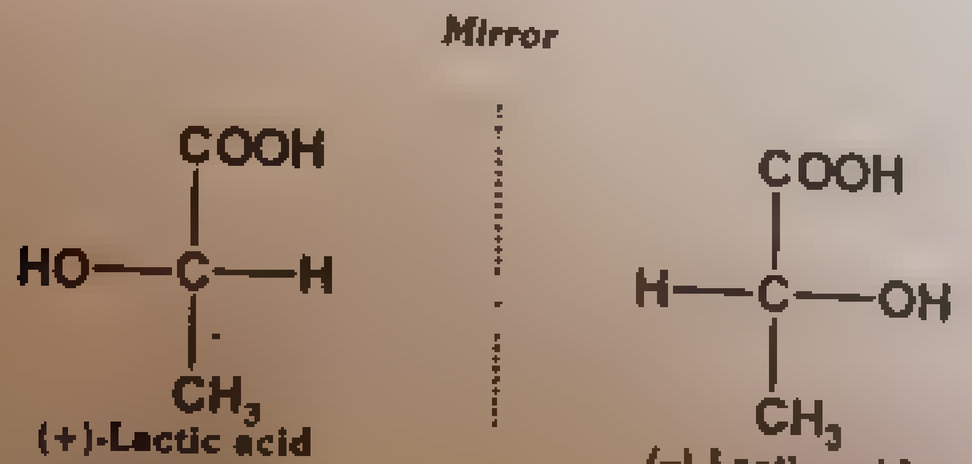
(a) Geometrical Isomerism or cis-, trans-isomerism: Example



cis-2-Butene trans-2-Butene

(b) Optical Isomerism

C3 (H2C):

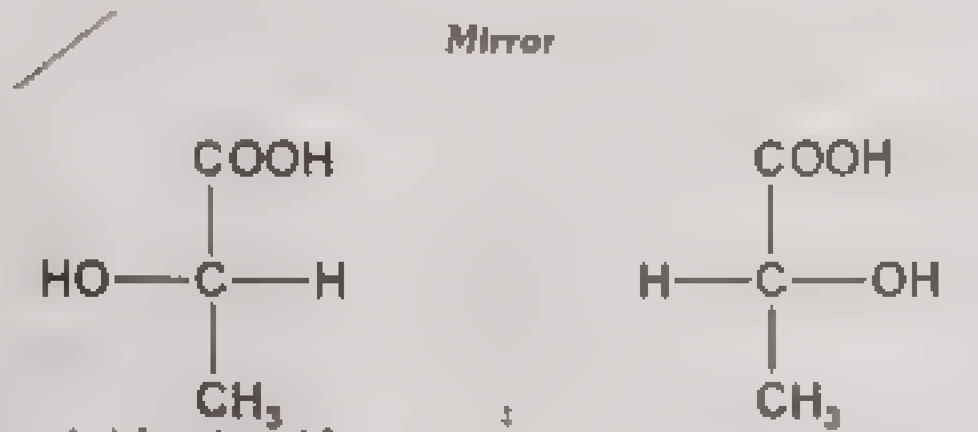


(+)-Lactic acid m.p. = 26°C (–)-Lactic acid m.p. = 26°C

7. How optical isomers arise?

- An asymmetric molecule has non superimposable mirror image. Such a molecule shows optical activity. It is also called a chiral molecule.
- The optically active compound can exist in two isomeric forms which rotate the plane polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical isomerism.
- The optical isomers have same atoms and same connectivity of atoms. However they differ in spatial (3D) arrangement of atoms.

Example:



(+)-Lactic acid m.p. = 26°C

(−)-Lactic acid m.p. = 26°C

8. What are conjugated bonds formed?

The word "**conjugation**" is derived from a Latin word that means "*to link together*".

In organic chemistry, it is used to describe the situation that occurs when pi systems are "linked together". Thus, an "**extended**" pi system exists over a longer series of atoms (e.g. C=C-C=C or C=C-C=O etc.)

Example:

$$\overset{1}{H_2C}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

1,3-Butadiene

9. Why alkenes are more reactive than alkynes?

- Both alkenes and alkynes contain pi bonds. The electrons of pi bond are exposed to attack by electrophiles.
- In alkynes, a triple bond is present. Due to high electrons density between carbon atoms, the C≡C triple bond is shorter (1.20 Å) than the C=C double bond (1.33 Å).
- Due to shorter bond length, the pi-electrons of a triple bond are less exposed and less reactive than alkenes towards electrophilic reagents.

10. Justify the given order of reactivity? Alkenes > Alkynes > Alkanes

- In alkanes, only sigma bond is present, which is difficult to break. Hence alkanes are least reactive.
- Both alkenes and alkynes contain pi bonds. The electrons of pi bond are exposed to attack by electrophiles.
- In alkynes, a triple bond is present. Due to high electrons density between carbon atoms, the C≡C triple bond is shorter (1.20 Å) than the C=C double bond (1.33 Å). Thus pi electrons of a triple bond are less exposed and less reactive than alkenes towards electrophilic reagents.
- Thus general order of reactivity towards electrophilic reagent is

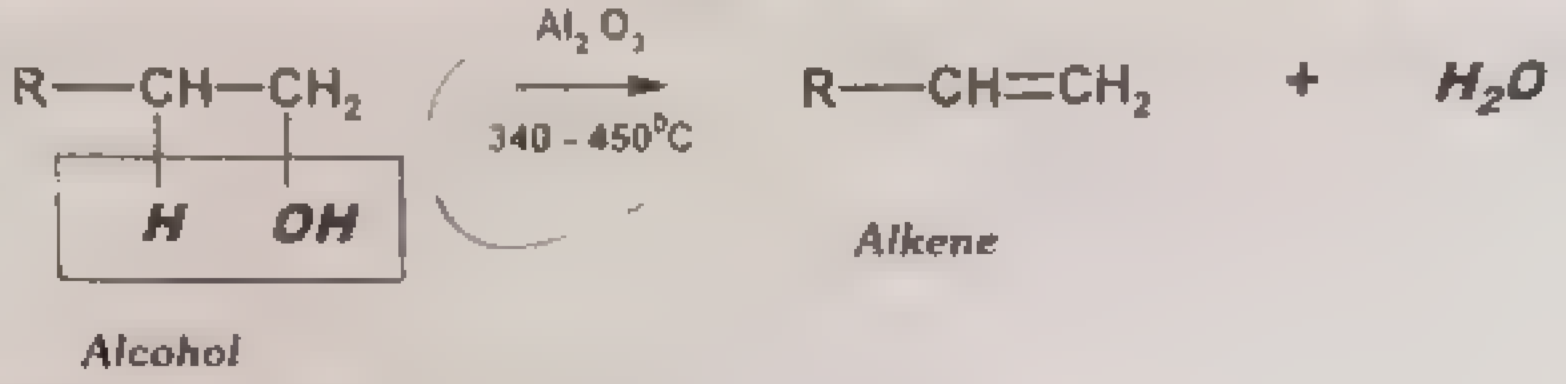
  Alkenes > Alkynes > Alkanes
- However, alkynes are more reactive than alkenes towards nucleophilic reagents.

11. What is meant by dehydration of alcohols?

[illegible] called dehydration

Example

When vapors of alcohol are passed over heated alumina, dehydration takes place with the formation of an [illegible]



- Other dehydrating agents used are P_4O_{10}, H_2SO_4, H_3PO_4
- The ease of dehydration of various alcohols is in the order

  Tertiary alcohol > secondary alcohol > primary alcohol

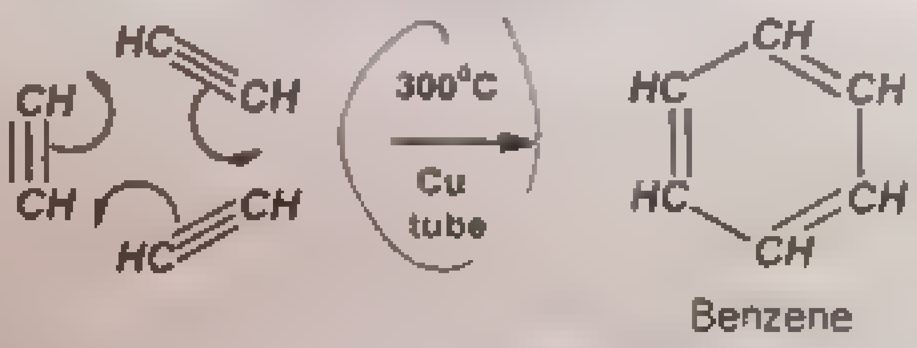
12. What are polymerization reactions?

- Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.
- Ethene polymerizes to polythene at 400 °C at a pressure of 100 atm

- Good quality of polyethylene is also produced by polymerization of ethene in the presence of aluminium triethyl $[Al(C_2H_5)_3]$ and titanium tetrachloride ($TiCl_4$) catalysts

13. How will you convert acetylene into benzene?

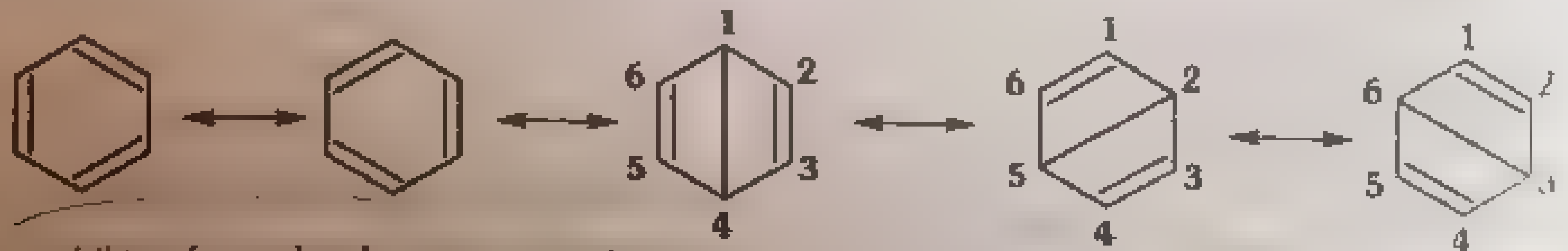
When acetylene is passed through a copper tube at 300°C it polymerizes to benzene



14. What is resonance?

The possibility of different pairing schemes of valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures".

Example: The following different pairing schemes of the fourth valence, the p-electrons of carbon are possible in benzene. This gives the following resonating structures of benzene



- The stability of a molecule increases with increase in the number of its resonance structures, of benzene is chemically quite stable.
- The actual structure of benzene is a resonance hybrid of all five structures

[illegible]

Examples

[illegible]

Q3. Give detailed answers to the following questions

1. [illegible]

2. (a) How will [illegible]

(i) an alkyl halide

[illegible]

$CH_3-CH_2-CH-CH_2$ [illegible]

(ii) Alcohols

[illegible]

(iii) Electrolysis of [illegible]

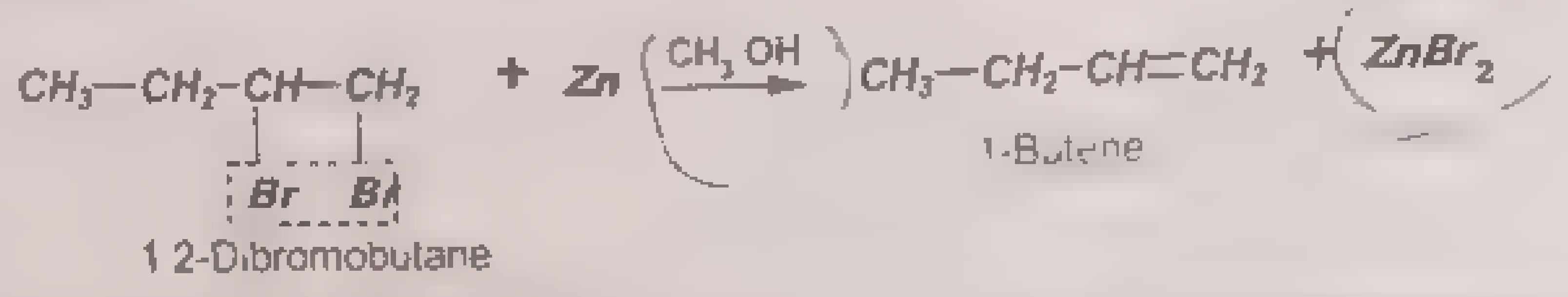
When aqu[illegible]

The reaction is [illegible]

[illegible]

(iv) vic-Dihalides

Vicinal dihalides have two halogen atoms on adjacent carbon atoms.
1,2-dibromobutane is a vicinal dihalide. When it is treated with Zn in alcoholic solvent or acetic acid, it gives 1-butene.



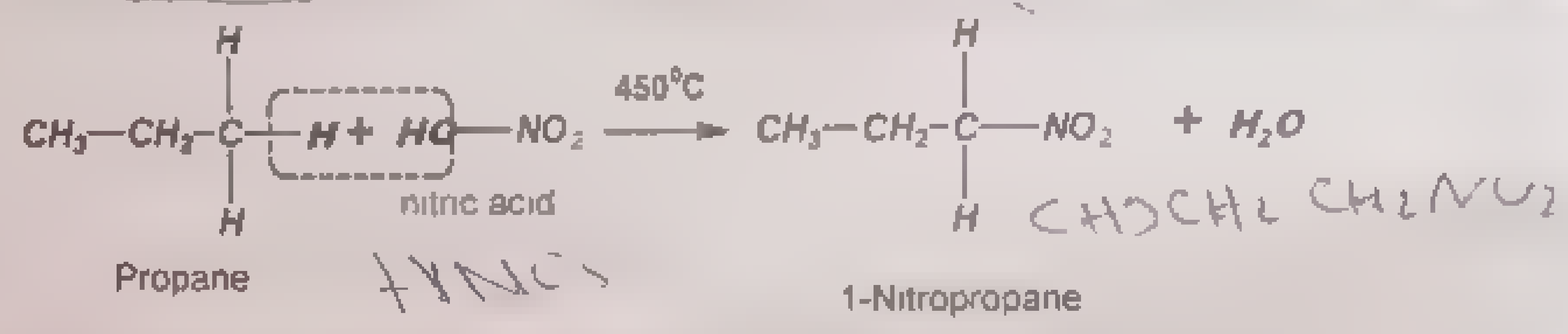
(b) What products is formed when n-propane undergo following reactions?

(i) Combustion

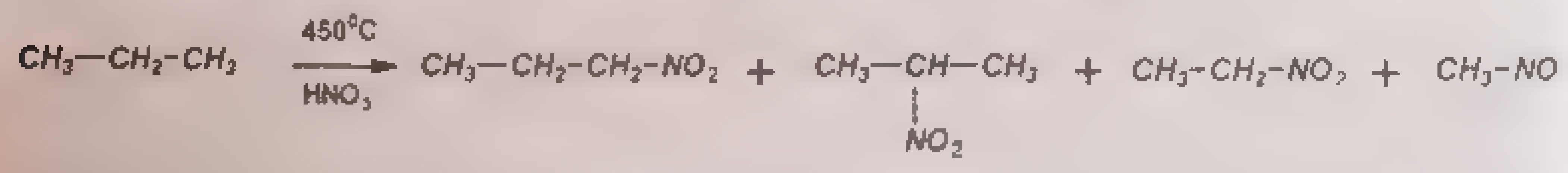
$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + \text{heat}$$

(ii) Nitration

n-Propane reacts with nitric acid in vapour-phase under drastic conditions at 400-500°C to give n-propane...

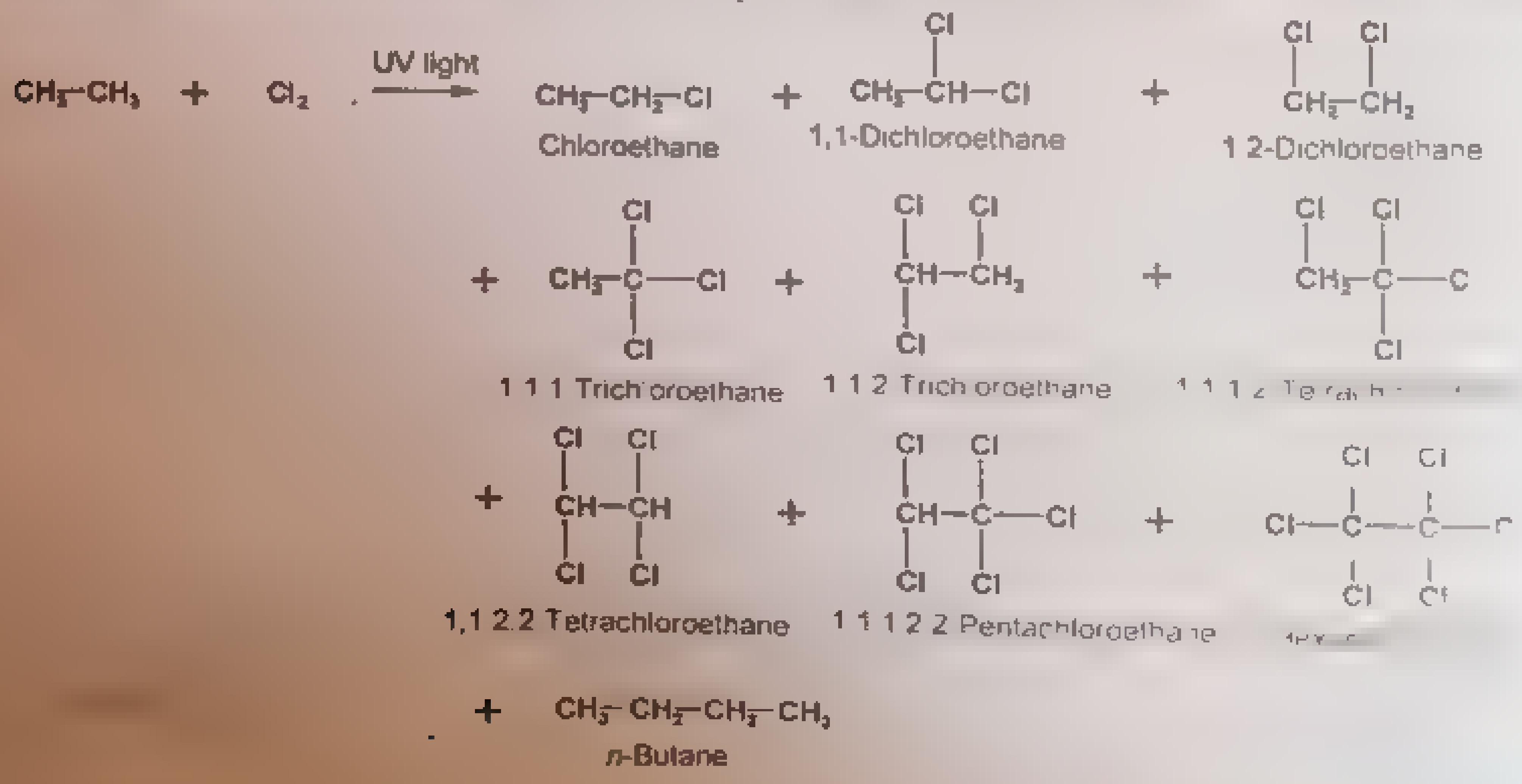


However, under drastic conditions, the molecule of n-propane is broken down and form all possible nitroalkanes.



3. (a) When ethane reacts with Cl_2 in UV light the mixture of products is formed. Give the detail of reaction with mechanism and all types of products.

Ethane reacts with Cl_2 in UV light to give a mixture of products. The reaction occurs by free radical mechanism. This reaction is called radical substitution reaction. The products of the reactions are



Mechanism: Free Radical Substitution

Initiation step

Step – 1 $\quad Cl-Cl \xrightarrow[UV]{h\nu} Cl^{\bullet} + Cl^{\bullet}$

Propagation steps

$$CH_3-CH_2-H + Cl^{\bullet} \longrightarrow CH_3-\dot{C}H_2 + HCl$$

Ethyl free radical

$$CH_3-\dot{C}H_2 + Cl-Cl \longrightarrow CH_3-CH_2-Cl + Cl^{\bullet}$$

- These two steps are repeated over and over again. Thus all hydrogens of ethane are replaced by chlorine atoms. The hydrogen atoms are replaced one by one

Termination step

$$CH_3-\dot{C}H_2 + Cl^{\bullet} \longrightarrow CH_3-CH_2-Cl$$

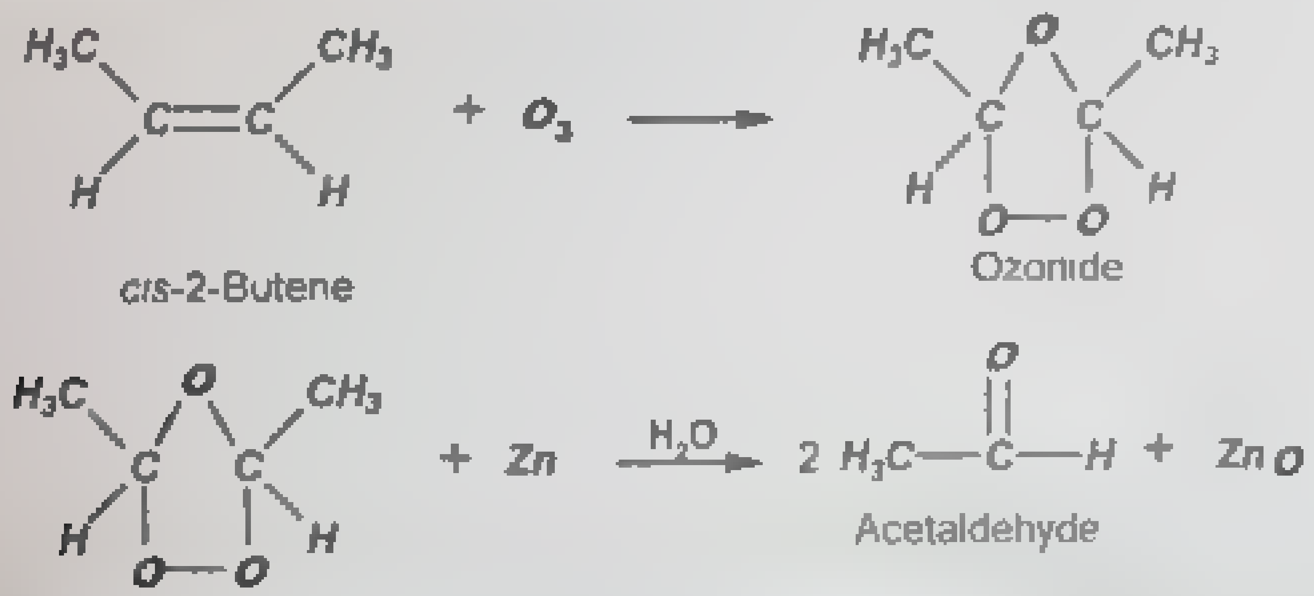
$$CH_3-\dot{C}H_2 + H_2\dot{C}-CH_3 \longrightarrow CH_3-CH_2-CH_2-CH_3$$

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

(b) *A compound when treated with Zn in methanol, the alkene is formed. When alkene is ozonolysed the acetaldehyde is formed as the major product. Explain reactions, give name and structure of the compound.*

$$H_3C-\underset{Br}{CH}-\underset{Br}{CH}-CH_3 + Zn \xrightarrow{CH_3OH} H_3C-CH=CH-CH_3 + ZnBr_2$$

2,3-Dibromobutane $\qquad$ 2-Butene



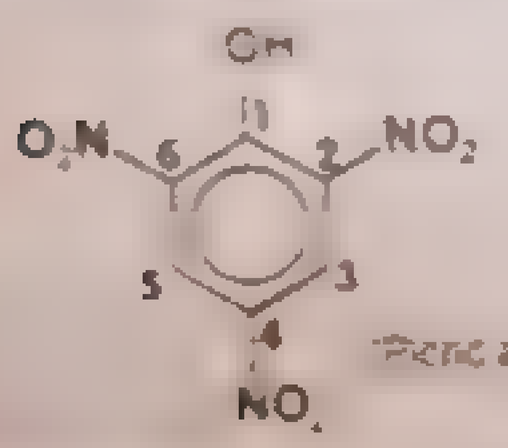
4 (a) *How will you prove that benzene has cyclic structure?*

Solved on Page 200

6. ... electrophilic substitution reactions of benzene with mechanism

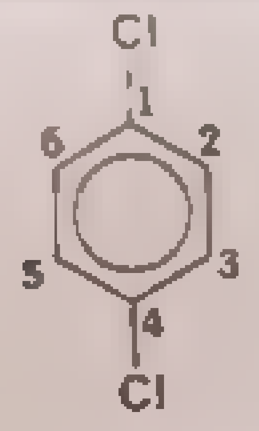
7. Write the structural formulas for the following benzene derivatives

(a) 2,4,6-Trinitrophenol

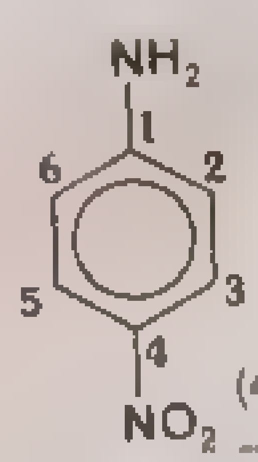


(Picric acid)

(b) 1,4-Dichlorobenzene

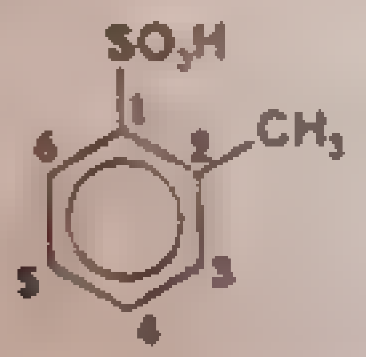


(c) 4-Nitrophenylamine

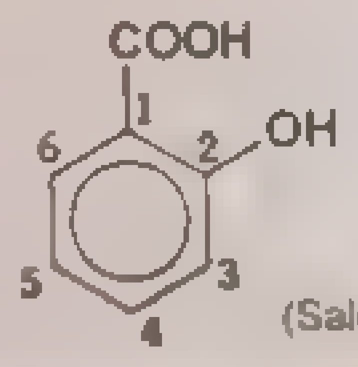


(4-Nitroaniline)

(d) 2-Methylbenzenesulphonic acid

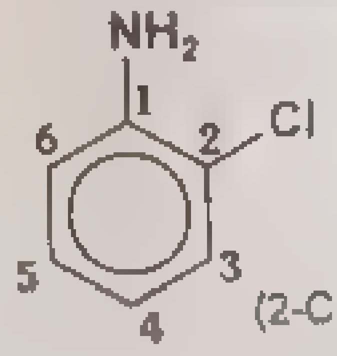


(e) 2-Hydroxybenzoic acid



(Salicylic acid)

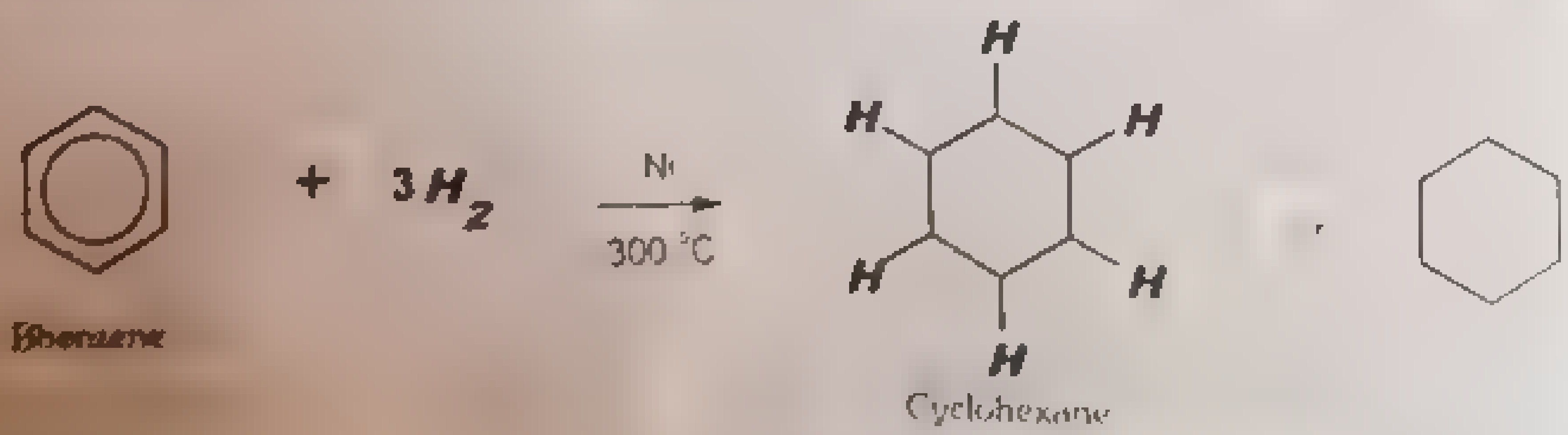
(f) 2-Chlorophenylamine



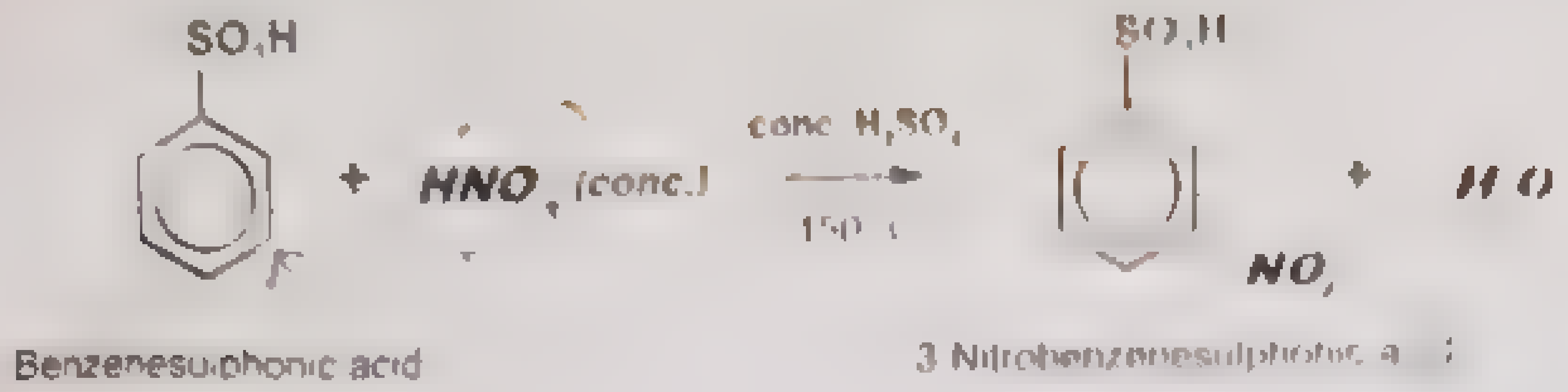
(2-Chloroaniline)

8. Predict the major products of the following reactions.

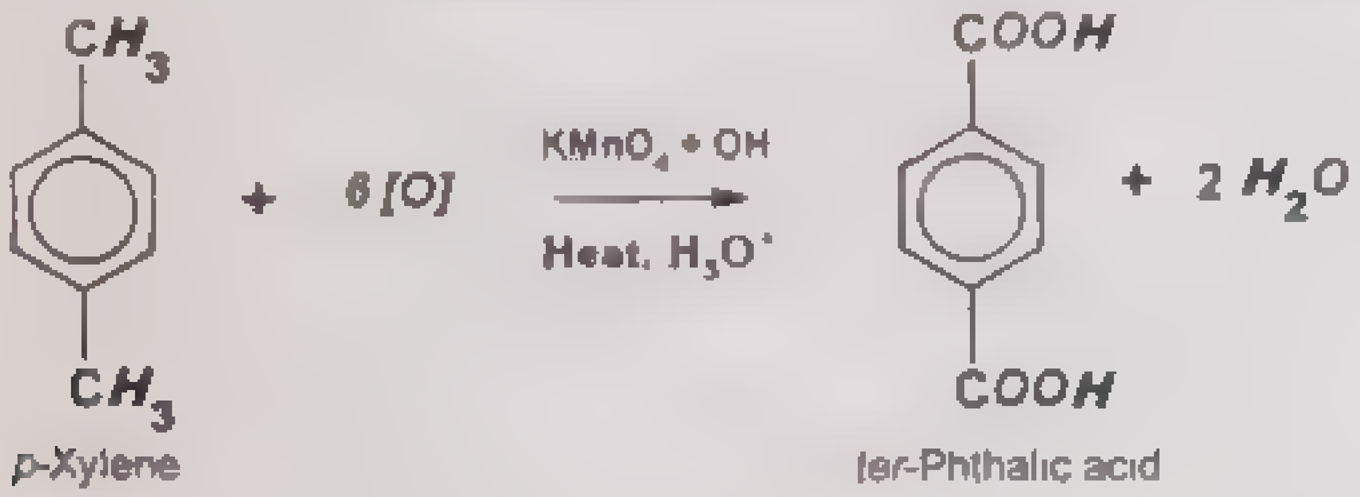
(a)



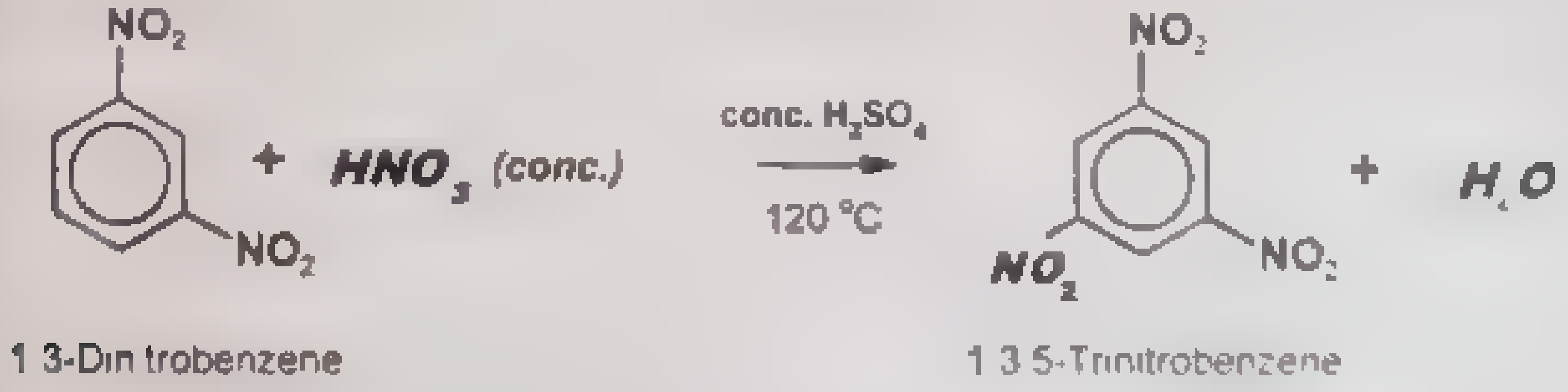
(b)


SO$_3$H
+ HNO$_3$ (conc.)
conc. H$_2$SO$_4$
NO$_2$
Benzenesulphonic acid

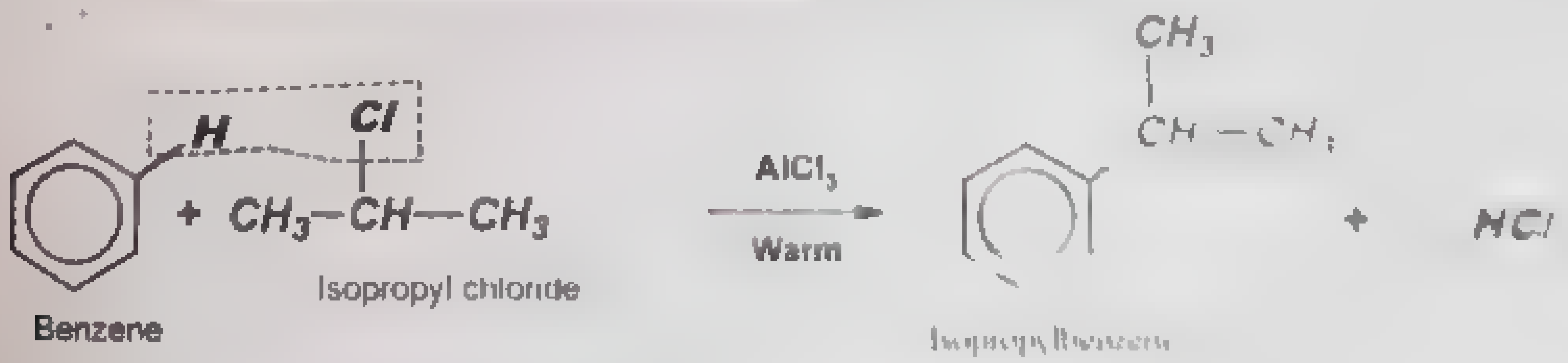
(c)


CH$_3$
+ 6 [O]
KMnO$_4$ + OH
Heat, H$_3$O$^+$
COOH
+ 2 H$_2$O
CH$_3$
p-Xylene
COOH
ter-Phthalic acid

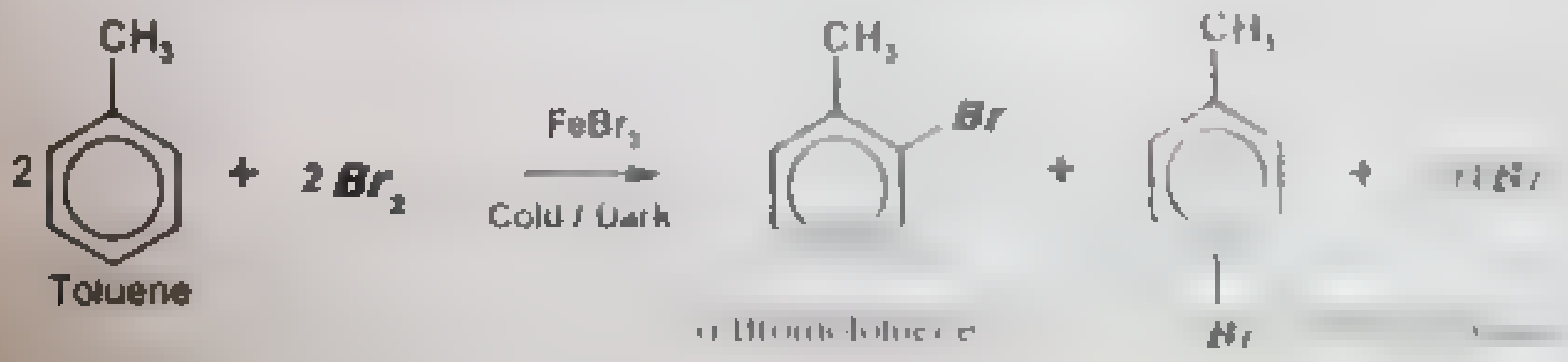
(d)


NO$_2$
+ HNO$_3$ (conc.)
conc. H$_2$SO$_4$
120 °C
NO$_2$
+ H$_2$O
NO$_2$
1 3-Dinitrobenzene
NO$_2$
NO$_2$
1 3 5-Trinitrobenzene

(e)

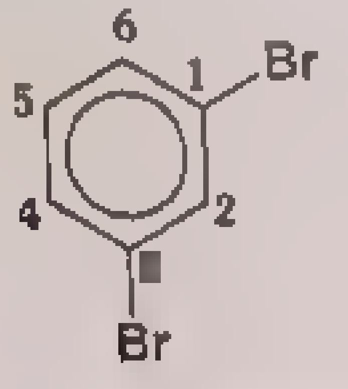

H
Cl
+ CH$_3$—CH—CH$_3$
Benzene
Isopropyl chloride
AlCl$_3$
Warm
CH$_3$
CH — CH$_3$
+
HCl

(f)


CH$_3$
2
+ 2 Br$_2$
Toluene
FeBr$_3$
Cold / Dark
CH$_3$
Br
+
CH$_3$
+
Br

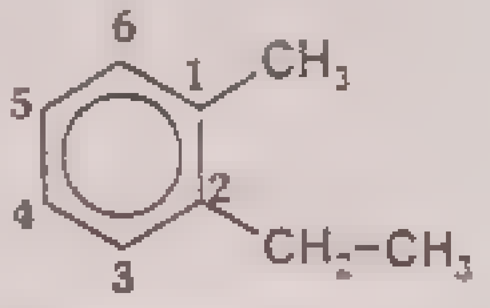
9 *Name the following benzene derivatives*

(a)



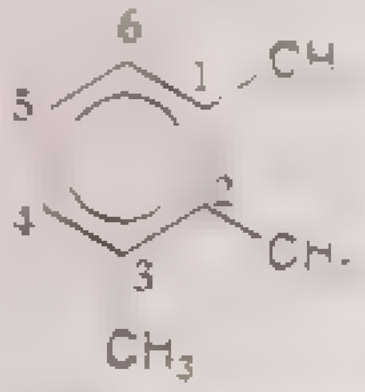
1,3-D bromobenzene

(b)



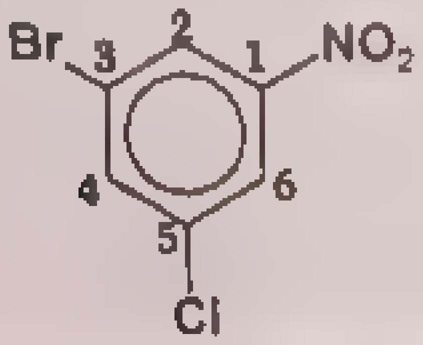
2-Eth[illegible]toluene

(c)



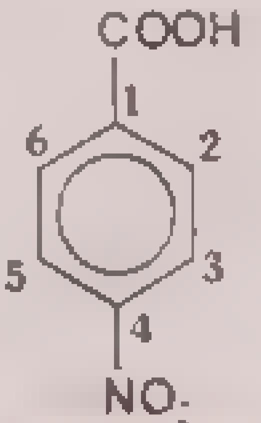
[illegible]

(d)



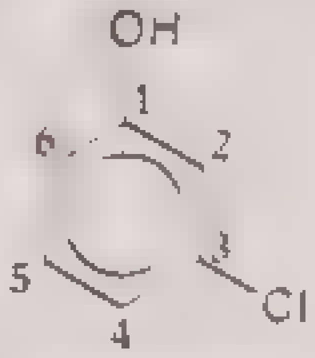
3-Bromo-5-chloronitrobenzene

(e)



4-Nitrobenzoic acid

(f)



[illegible]

Why Groups are ortho/para and meta-directors?

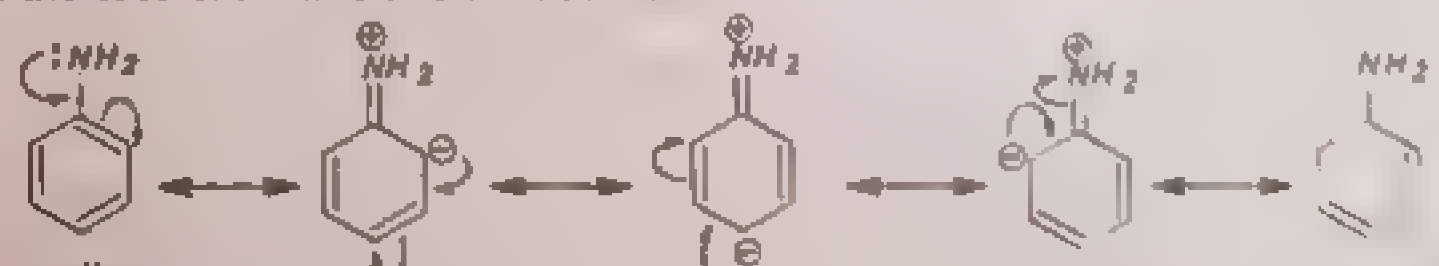
Resonance Effect:

The decrease in electron density at one position is a molecule, with corresponding increase in ele[illegible] density at some other position is called Resonance Effect or Mesomeric Effect.

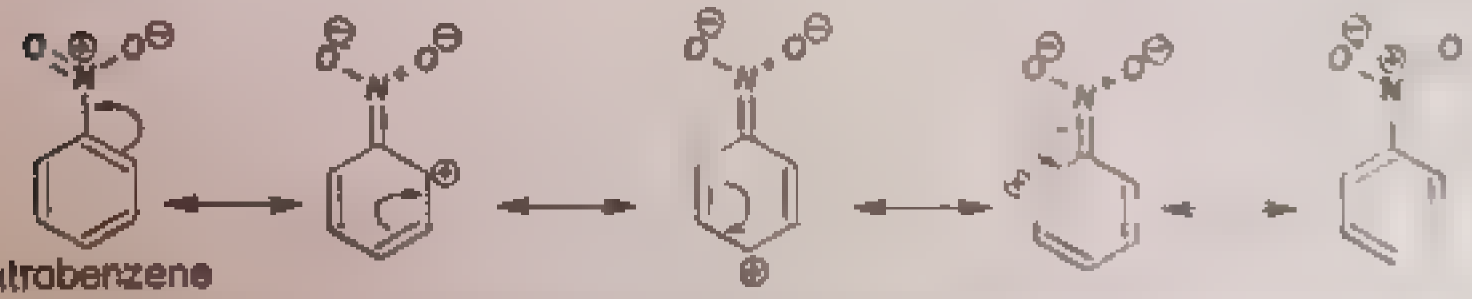
Examples

In delocalized chemical systems, electron density spread over various at[illegible]

e.g. consider the case of Aniline and nitrobenzene



aniline



nitrobenzene

Thus, NH_2 donates electron to the ring while NO_2 group withdraws electrons from the ring

Following things should be noted.

- *In case of aniline, the negative charge comes at ortho para positions. So [illegible] positions. So, NH_2 group is an ortho/para director.*
  Moreover, since the electron density is increased on the ring, so it is an acti[illegible]
- *In case of nitrobenzene, the positive charge comes at ortho para positions. So [illegible] these positions. Rather it will attack on meta-positive. So, NO_2 group is a meta[illegible]*
  Moreover, since the electron density is decreased on the ring, so it is an deacti[illegible] group
- *Similarly others can also be explained.*

TopStudy

TEST YOUR SKILLS

Time 25 Minutes

(iv) Benz...

A. Detect...

v) The ...

(vi) Acetylene ...

A. White ppt. ...

(vii) Acidic h...

A. Acetylene

(ix) Ethylene ...

(x) Presence of double ...

A. Unsaturation

(xi) Addition of HCN to eth...

(xii) Which hydrocarb...

A. Meth...

(xiii) The product form...

A. Benzene

(xiv) Sodalime is

A. NaOH B. ...

(xv) Vinly acetylene ...

A. Poly...

(xvi) Mustarad gas is a

A. gas

(xvii) To which of the followin...

A. $CH_3CH-CHCH_3$ B. ...

Time: 2:35 Hours

Q2. Attempt any FOURTEEN parts. The ...

(i) In Ethyne and other terminal ...

a. Why 1-alkynes ...

b. Write a reaction to show the ...

(ii) Give mechanism of addition of ...

(iii) a. Define Markownikov's ...

b. Complete the following react...

(iv) Both alkenes and alkyn...

a. How will you differen...

b. ...

c. ...

(v) How is 2-Butene prepared [illegible]

a. [illegible]

Briefly explain the difference between [illegible]

ii. How will you [illegible]

a. [illegible]

(vii) [illegible]

a. Write the [illegible]

b. Write the [illegible]

Complete the [illegible]

a. propene $\longrightarrow$? $\longrightarrow$?

b. propyne $\longrightarrow$?

c. Ethane → Ethene → Ethyne

(x) a. Why alkanes are [illegible]

b. What are [illegible]

(xi) a. What is meant by [illegible]

b. Write the structural [illegible]

(xii) a. What is the effect of branching on boiling point of alkanes? 01

b. How many ethene be [illegible] 01

c. Alkenes usually undergo addition reactions while alkanes do not why? 01

(xiii) How does Ethyne react with 03

a. $AgNO_3$, NH_4OH [illegible]

(xiv) a. Justify the given order of reactivity [illegible] 2

Alkenes > alkynes

b. What is conjugation. 01

(xv) a. Why alkanes are called paraffins?

b. Why alkenes are called olefins?

c. What is meant by dehydration of alcohols?

(xvi) a. How do you convert alkynes into cis and trans alkenes 2

b. What is Baeyers reagent and Baeyers test? 01

(xvii) a. How will you distinguish between ethane and ethyne 1

b. How mustard gas is prepared 01

c. How will you distinguish between 1-butyne and 2-butyne by chemical test

(xviii) a. What is meant by optical activity?

b. What is tautomerism? Give examples

(xix) a. How aldehydes or ketones are produced from alkenes? 2

b. What is a polymerization reactions? 1

Section - C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

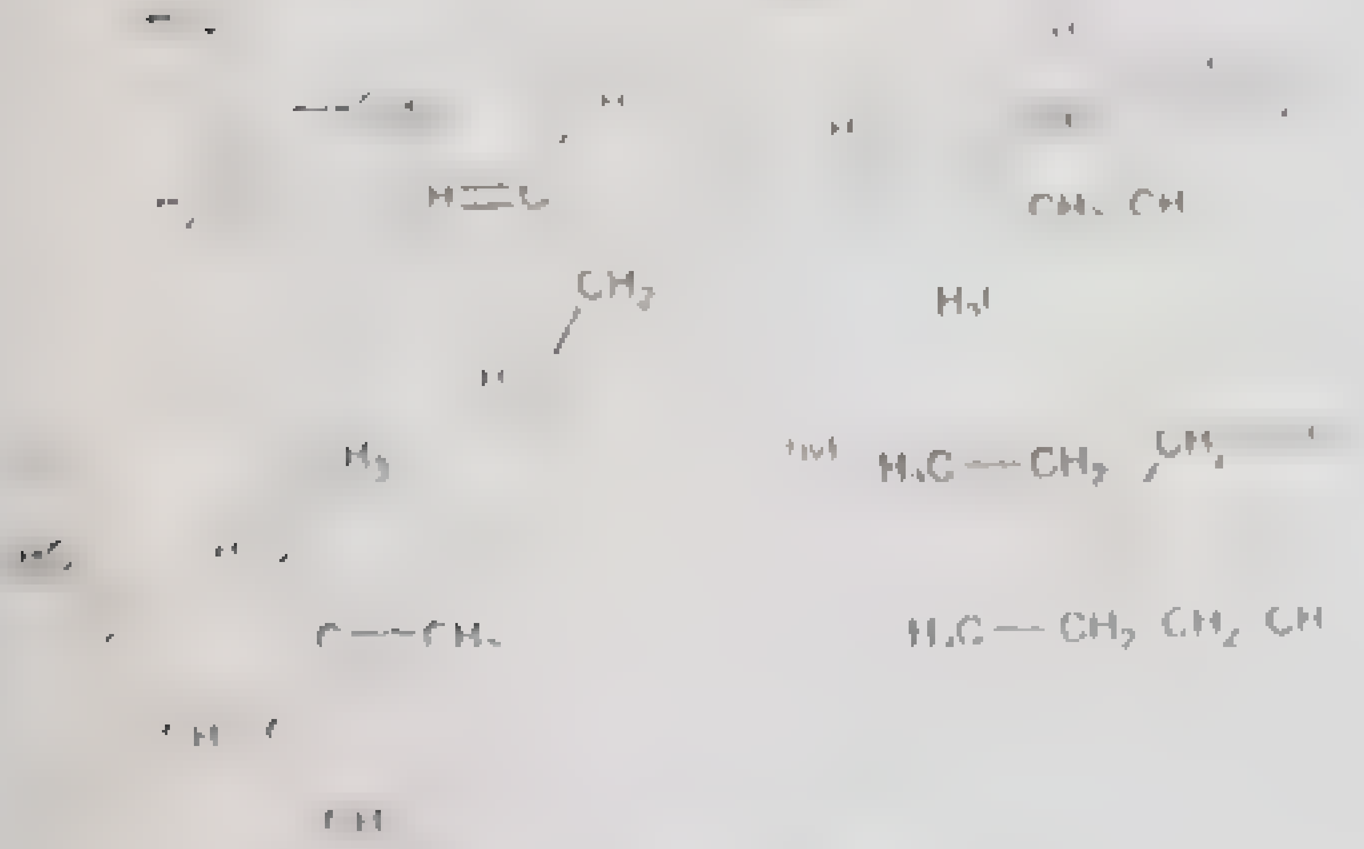
Q. 3 a. How will you prepare 1-butene from?

(i) An alkyl halide (ii) Alcohols

iii) Benzene (iv) a germinal dihalide iv. Et

Q.8

Q.9



Complete the following sequence of the reaction

TEST YOUR SKILLS (AROMATIC COMPOUNDS)

OBJECTIVE

Time 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Q1 Circle the correct option i.e. A/B/C/D Each part carries one mark

(i) The conversion of n – hexane into benzene by heating in the presence of Pt is called
A isomerism **B. aromatization** C dealkylation D rearrangement

(ii) Catalyst used for Friedal craft's reaction is
A HNO_3 **B. $AlCl_3$** C $BeCl_2$ D NaCl

(iii) Benzoic acid formed by oxidation of
A Toluene B Ethyl benzene C n-propyl benzene **D All**

(iv) C-C bond length in benzene is
A 1.34 Å B 1.20 Å **C. 1.40 Å** D 1.54 Å

(v) Aromatic compounds burn with sooty flame because
A. High percentage of hydrogen B Ring structure
C. High percentage of carbon D They resist reaction with air

(vi) Resonance structure of a molecule should have
A Same number of paired electrons B Identical arrangement of atoms
C Nearly same energy content **D. All of these**

(vii) In which one of the following compounds the benzene rings are isolated
A Naphthalene B Anthracene C Phenanthrene **D. Diphenyl methane**

(viii) Benzene can not undergo
A. Elimination B Substitution C Oxidation D A...

(ix) Nitrating agent in nitration of benzene is
A HNO_3 **B. NO_2^+** C NO_3^- D ...

(x) Benzene on catalytic oxidation at 500°C with V_2O_5 ...
A. Benzoic acid **B. Maleic anhydride** C M...

(xi) Amongest following, strongest o p directing group
A – Cl **B. –OH** C ...

(xii) The effect of substituent Cl in electrophilic substitution ...
A. o,p-director and deactivating B o p director a...
C m-director and activating D m director and ...

(xiii) The aromatic ring can be hydrogenated by using the catalyst
A. Pt B Pd C Rh D N...

(xiv) Which xylene gives only one monobromo derivative
A. Para B Meta C Ortho D N...

(xv) Benzene is prepared from cyclohexane by the process called
A. Hydrogenation B Dehydration **C. Dehydrogenation** D ...

(xvi) In which one of the following compounds ...
A. Toluene **B. Nitrobenzene** C Benzene D Ph...

(xvii) Shape of benzene molecule is
A. Pyramidal B Linear Plane C trigonal **D. hexagonal Planar**

SUBJECTIVE

Time: 2 35 Hours **Total Marks Section B and C ...**

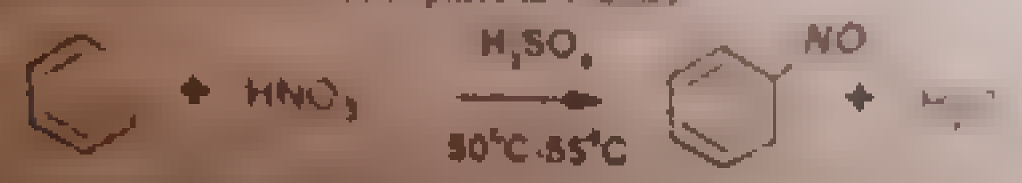
Section – B (Marks 42) (14 × 3 = 42)

Q2 Attempt any FOURTEEN parts. The answer to each part should not exceed ...

(i) The carbon-carbon bond length in Benzene is different ...
a. Which compound contains the longer bond
b. Give reason for your answer

(ii) Aromatic compounds undergo Electrophilic Substitution ...
a. Explain why Nitration of Toluene is easier than th...
b. How would you convert Toluene into T...

(iii) Nitration of benzene takes place as follows



a. Which is the nitrating agent and how it is produced
b. Write complete mechanism for the above ...

[illegible] the truth with the help of examples

a. [illegible]

b. [illegible]

[illegible]

a. [illegible] + [illegible] $\longrightarrow$?

b. [illegible] + [illegible] $\longrightarrow$?

a. What are [illegible]?

b. What are [illegible] aromatic hydrocarbons?

c. What are aryl groups

a. Give reactions which show that benzene has a cyclic structure with three alternate double bonds 02

b. [illegible]

a. Why [illegible] structure has greater contribution towards the actual structure of benzene? 02

b. [illegible] 01

a. Why [illegible] bonds are of equal length in benzene

b. Give [illegible] which shows that benzene is a saturated compound 02

a. Benzene usually undergoes electrophilic substitution reaction and not addition reaction, why? 02

b. What [illegible] when benzene react with Cl_2 in the presence of [illegible] 01

a. Write [illegible] benzene

b. [illegible] ortho and para nitrotoluene while nitration of nitrobenzene gives meta dinitro benzene. Explain 1.5

a. What [illegible] the oxidation of toluene and ethyl benzene? 02

b. Why [illegible] than benzene towards electrophiles?

c. What [illegible] 01

a. How [illegible] benzene?

b. Give general mechanism of electrophilic substitution reaction of benzene

a. What are Friedal and Craft reactions?

b. Write down IUPAC name of o-xylene and p-xylene?

Why Dewaar structures of benzene are considered as unstable?

a. How benzene is obtained from (A) acetylene (B) n-hexane

b. Give all possible isomers of xylenes

a. Justify the given order of reactivity Alkenes > Benzene > Alkanes

b. What information was obtained from X-ray analysis of benzene

a. What are isolated and fused polycyclic hydrocarbons? Give example

b. What is Robinson structure of benzene?

Section C

Note: Attempt any TWO questions. All questions carry equal marks (2 × 13 = 26)

Q. 3. a. How will you prove that benzene has cyclic structure

b. Explain the structure of benzene according to Atomic orbital treatment

c. Why benzene is stable compound? Explain with [illegible]

d. How will you prepare benzene from?

(i) Alkanes (ii) Phenol (iii) Salt of benzoic acid

Q. 7. a. Explain the following electrophilic substitution reactions of benzene with [illegible]

(i) Halogenation (ii) Sulphonation [illegible]

b. Draw the structural formulas for the [illegible]

(i) p-Chlorobenzoic acid (ii) m-Di[illegible]

(iii) p-Dibenzyl benzene (iv) Benzoyl [illegible]

c. Name four meta directing groups

Q. 8. (a) What products are formed when benzene reacts with [illegible]

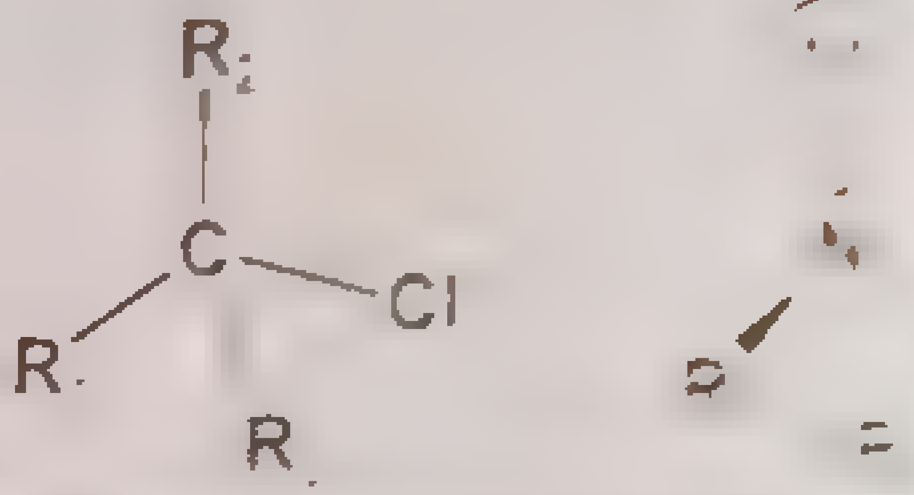
(i) Br_2 in presence of sunlight (ii) O_2 [illegible]

(b) Explain that how ortho and para [illegible]

(c) Define Resonance. Draw all the possible resonating structures [illegible]

What structure would you suggest best for representing [illegible]

CHAPTER # 17
ALKYL HALIDES AND AMINES



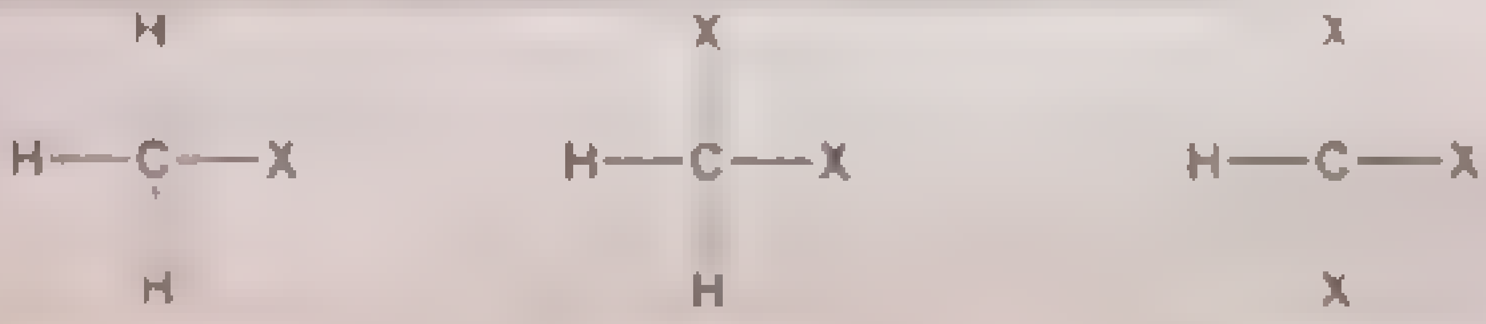
ALKYL HALIDE

INTRODUCTION

Alkyl halides are the compounds in which one hydrogen atom of Alkanes has ... halogen atom. They are also known as halogen derivatives.

TYPES

... molecule. M...



CLASSIFICATION OF ALKYL HALIDES

Alkyl halides are classified into primary, seco...

(I) Primary Alkyl Halides

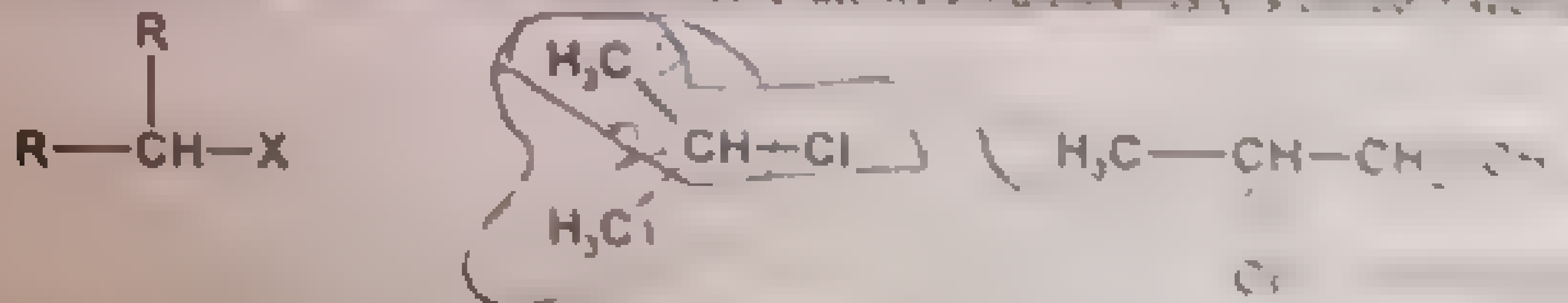
Alkyl halide in which halogen atom is attached with primary carbon ... A primary C-atom is attached to one or no carbon atom is called a primary C...

$R-CH_2-X$ $\quad$ CH_3-Cl $\quad$ CH_3-CH_2-Cl $\quad$ CH...

Methyl chloride $\quad$ Et...

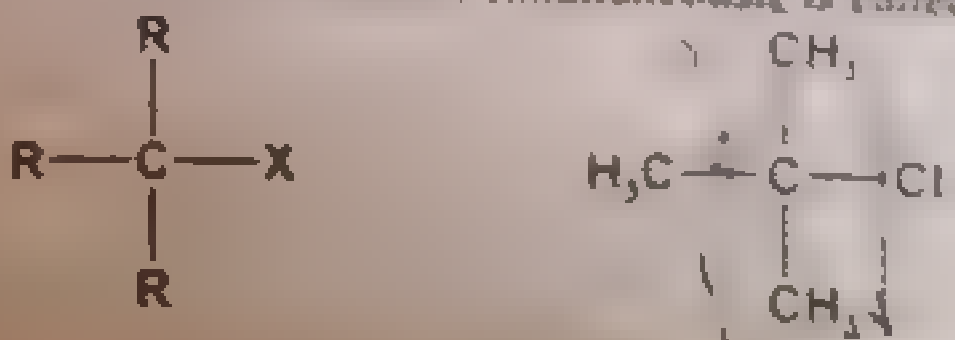
(II) Secondary Alkyl Halides

Alkyl halide in which halogen atom is attached with a secondary carbon ... halide. A Secondary C-atom is attached to two C-atoms ...



(III) Tertiary Alkyl Halides.

Alkyl halides, in which halogen atom is attached to a tertiary carbon ... A tertiary C-atom is attached to three C-atoms simultaneously is called a tertiary C...



2 Chloro 2 methyl propane

NOMENCLATURE:

i) Common System of Naming

Examples

CH_3-Cl Methyl chloride

CH_3-CH_2-Cl Ethyl chloride

$CH_3-CH_2-CH_2-Cl$

$CH_3-CH-Cl$ with CH_3

ii) IUPAC System of naming

1)

2)

3)

$CH_3-CH_2-CH_2-Cl$

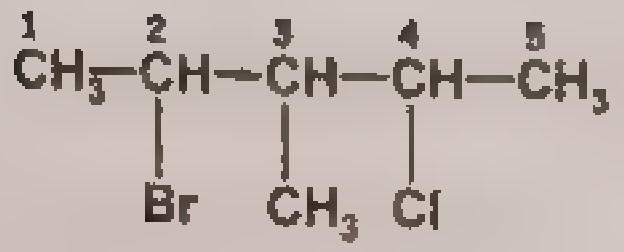
$\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-Cl$ (with CH_3 and Cl substituents shown)

$CH_3-CH_2-CH(CH_3)-CH_2-CH(Cl)-CH_3$

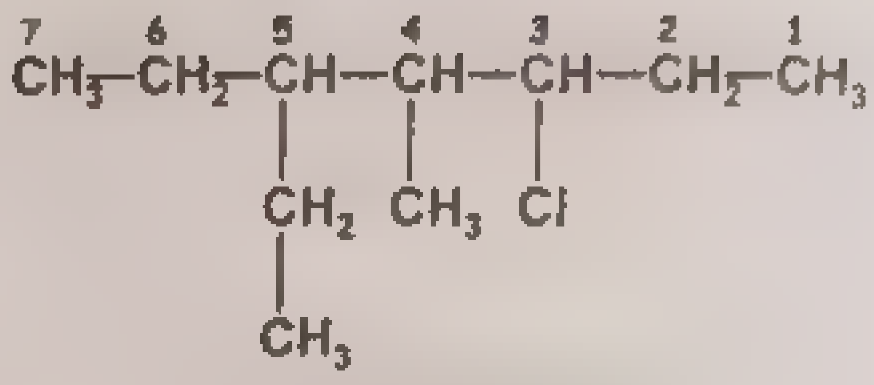
$CH_3-C(CH_3)_2-Cl$

2-Chloro-2-methylpropane

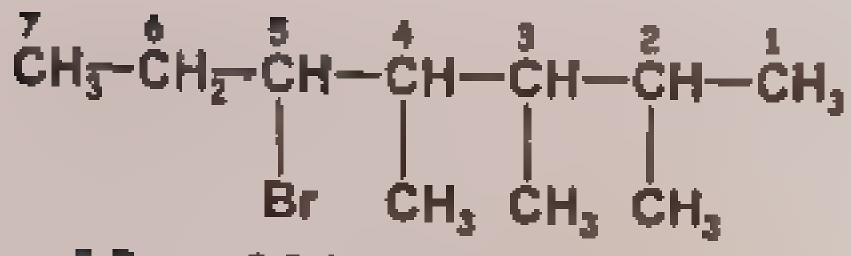
MORE PRACTICE



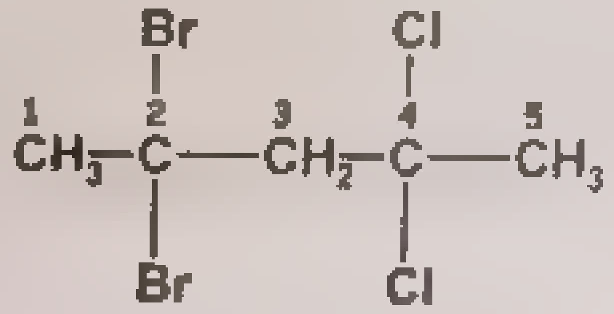
2-Bromo-4-chloro-3-methylpentane



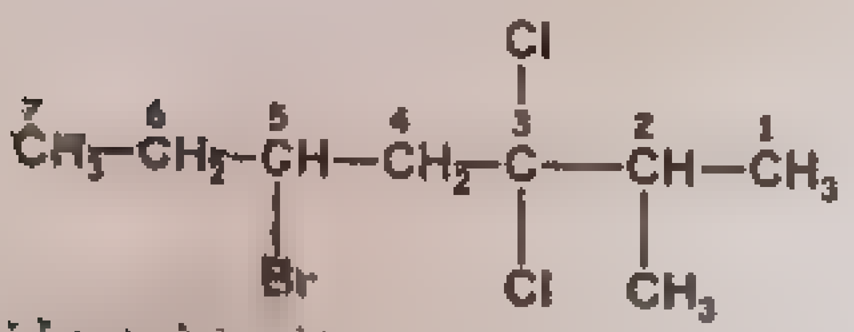
3-Chloro-5-ethyl-4-methylheptane



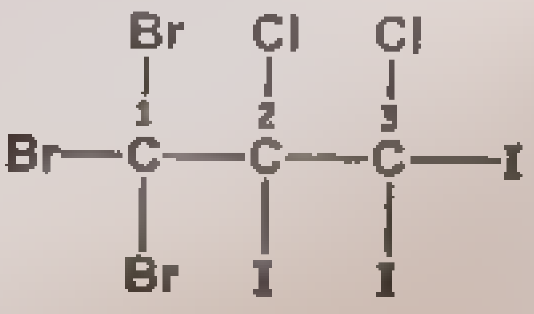
5-Bromo-2,3,4-trimethylheptane



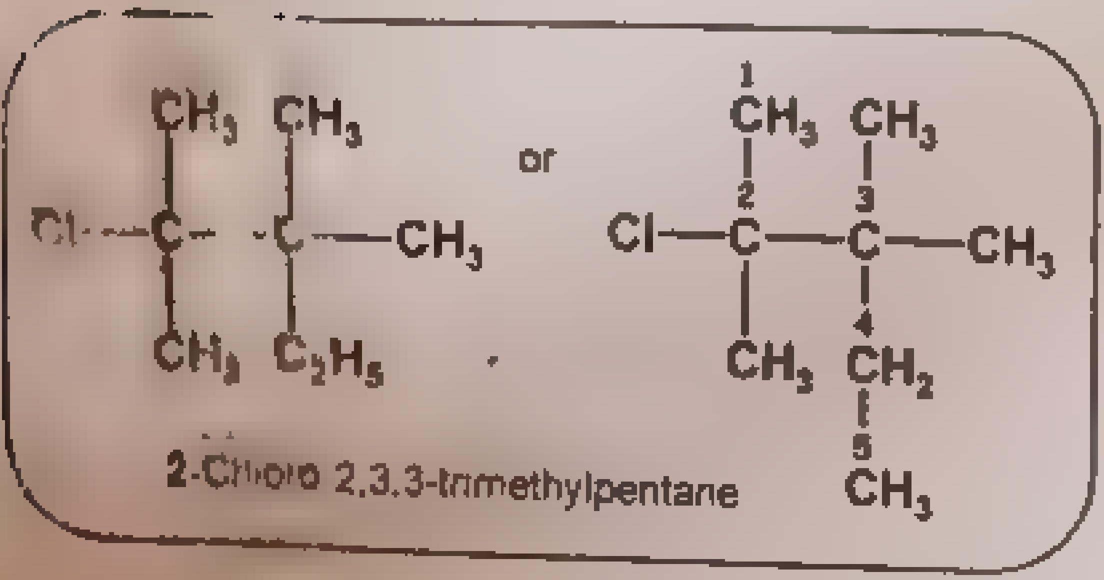
2,2-Dibromo-4,4-dichloropentane



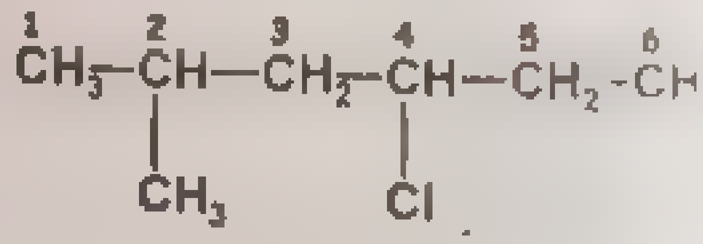
5-Bromo-3,3-dichloro-2-methylheptane



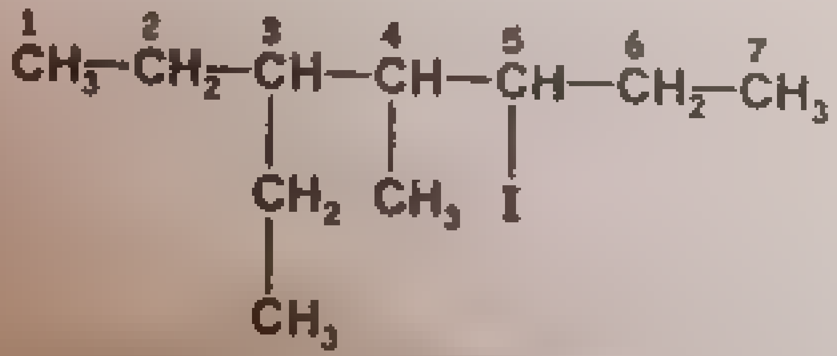
1,1,1-Tribromo-2,3-dichloro-2,3,3-triiodopropane



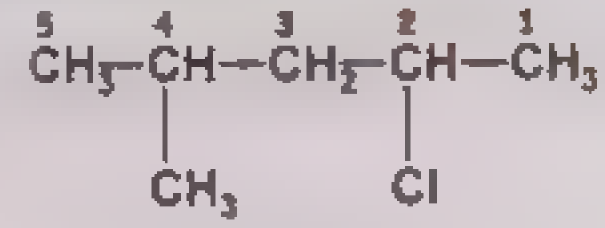
2-Chloro 2,3,3-trimethylpentane



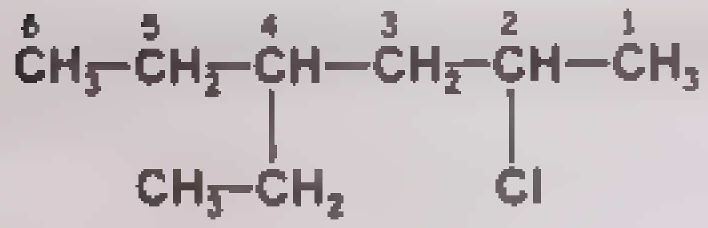
4-Chloro-2-methylhexane



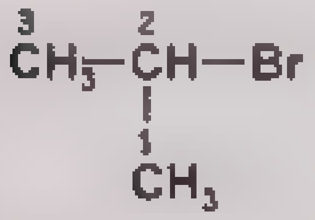
3-Ethyl-5-iodo-4-methylheptane



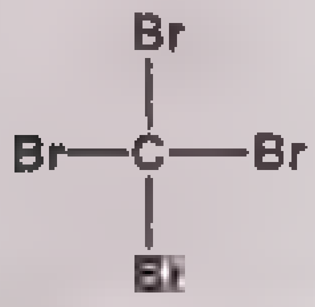
2-Chloro-4-methylpentane



2-Chloro-4-ethylhexane

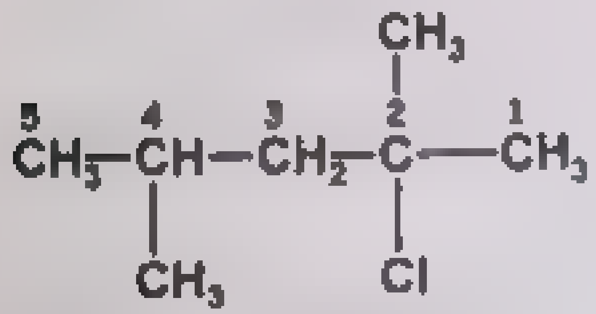


2-Bromopropane

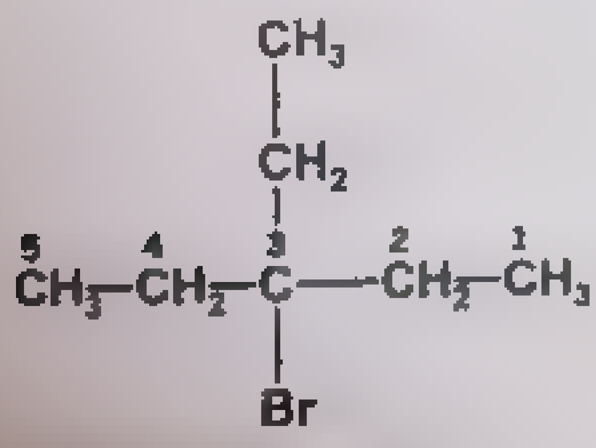


Tetrabromomethane

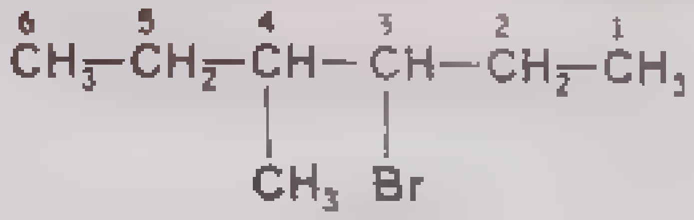
Dichloromethane



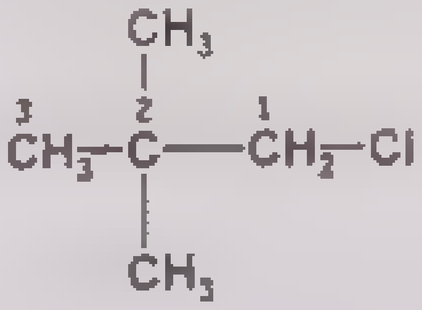
2-Chloro-2,4-dimethylpentane



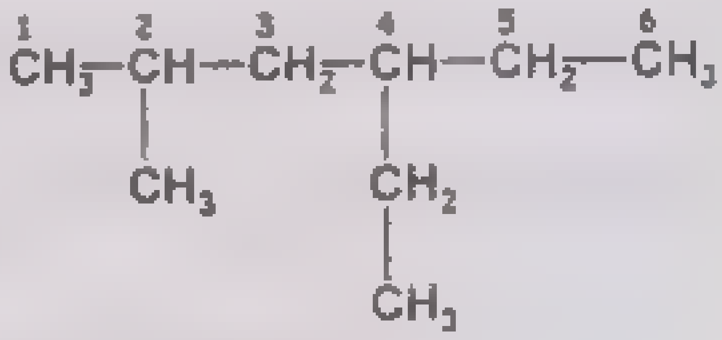
3-Bromo-3-ethylpentane



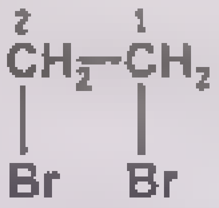
3-Bromo-4-methylhexane



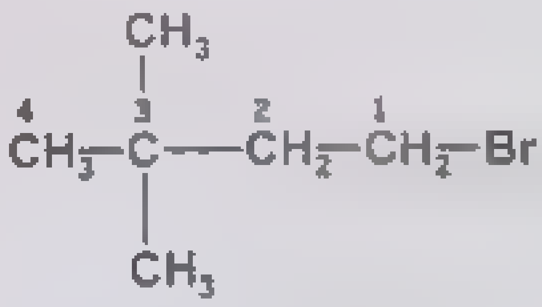
1-Chloro-2 2-dimethylpropane



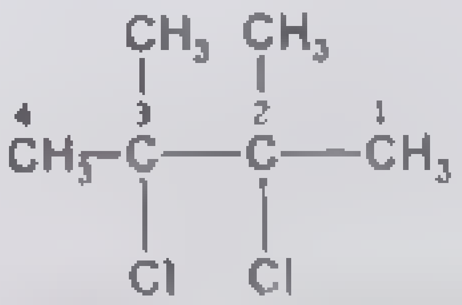
4-Ethyl-2-methylpentane



1,2-Dibromoethane



1-Bromo 3 3-dimethylbutane



2 3-Dichloro-2 3-dimethylbutane

PHYSICAL PROPERTIES

The alkyl halides contain a polar bond. Thus, it has higher melting points and b...

STRUCTURE

- The alkyl halide functional group consists of an sp^3-hybridized C atom bonded to a ... σ- bond
- The carbon halogen bonds are polar due to the electronegativity and polarizability ...

PREPARATIONS OF ALKYL HALIDES

Exercise Q3 (ii) Give three methods for the preparation of alkyl halides.

(1) Reaction of Alcohols with Hydrogen Halides

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the ... of $ZnCl_2$ as a catalyst

$$CH_3-CH_2-OH + H-X \xrightarrow{ZnCl_2} CH_3-CH_2-X + H_2O$$

(2) Reaction of Alcohols with other Halogenating agents ($SOCl_2$; PX_3)

(a) Alcohols react with thionyl chloride in pyridine as a solvent to give alkyl chlorides.
This is the best method because HCl and SO_2 are gases which escape out leaving behind the pure prod...

$$R-OH + SOCl_2 \xrightarrow{\text{pyridine}} R-Cl + SO_2 + HCl$$

(b) Phosphorous trihalides or phosphorous pentahalides react with alcohols to from alky halides

$$3\,CH_3-CH_2-OH + PBr_3 \longrightarrow 3\,CH_3-CH_2-Br + H_3PO_3$$

$$CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3 + HCl$$

(3) Halogenation of Alkanes

- Alkanes react with chlorine or bromine to give alky halides
- This reaction takes place in the presence of diffused sunlight or ultraviolet light

$$CH_3-CH_3 + Cl_2 \xrightarrow[\text{UV, light}]{h\nu} CH_3-CH_2-Cl + HCl$$

NOTE:

- This method does not give pure alkyl halides. Halogen derivatives containing two or m... atoms are also formed along with alkyl halides.

The detail mechanism of this reaction has already been discussed in Chapter # 16 (Radical Substitution)

REACTIVITY

Exercise Q3 (i) Discuss the reactivity of alkyl halides.

There are two main factors which control the reactivity of alkyl halides
(1) Bond polarity of C-X bond
(2) Bond energy of C-X bond

1. Bond Polarity

- The molecule of alkyl halide is polarized due to the greater ...

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

- Hence carbon acquires partial positive whereas halogens acquires partial negative charge. $-\overset{|}{\underset{|}{C}}^{\delta+}-X^{\delta-}$
- Halogen becomes nucleophilic in character ...
- The polarity order is R-F > R-Cl > R-Br > R-I

2. Bond Energy

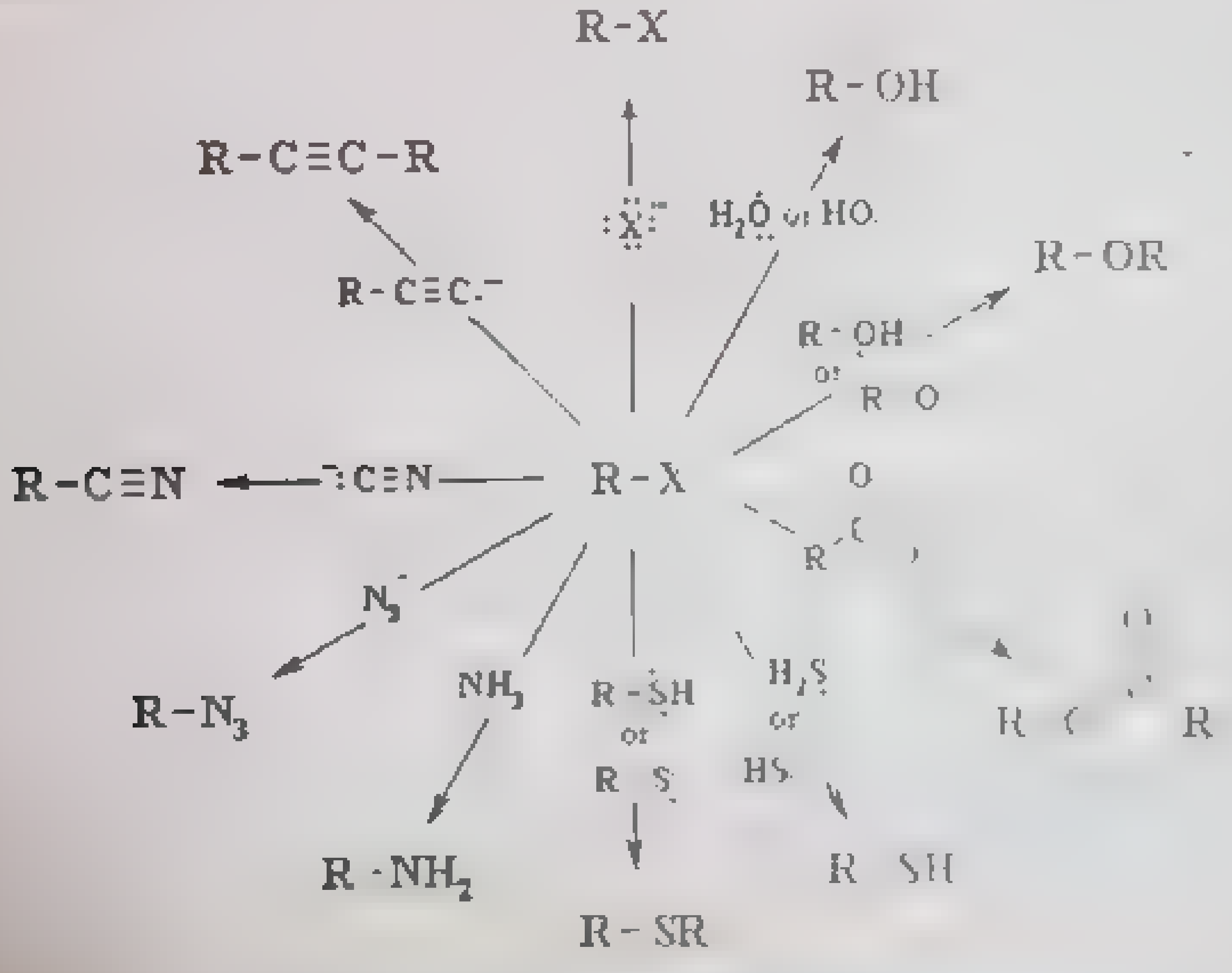
- Experiments have shown that the bond energy of C-X bond ... which decides the reactivity of alkyl halides, and not the polarity of the molecule.
- A study of bond energies of C-X bond shows that C-F bond is the strongest ... the overall order of reactivity of alkyl halides is:

  R-iodide > R-bromide > R-chloride > R-fluoride
- In fact the C-F bond is so strong that alkyl fluorides do not react ...

NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES

- Alkyl chlorides, bromides and iodides are good substrates for substitution reactions.
- A variety of nucleophiles can be used to generate a range of new functional groups.
- The following diagram reflects some of the more important reactions you may encounter.
- For practice, make sure you can draw the mechanisms that lead to these products.

Reactions Summary



IMPORTANT DEFINITIONS

Electrophile

Specie in search of negative charge is called an electrophile

Examples

NO_2^+ , Br^+ , CH_3^+ etc

Nucleophile

Specie in search of positive charge is called a nucleophile

OR ***A nucleophile is electron rich species that will react with an electron poor species***

It has a lone pair of electrons available for bonding or has negative charge

Examples

HO^-	Hydroxide ion	NH_2^-	Amino group
$C_2H_5O^-$	Ethoxide ion	Cl^-	Chloride ion
HS^-	Hydrogen Sulphide ion	Br^-	Bromide ion
SCN^-	Thiocyanate ion	NH_3	Ammonia
H_2O	Water		

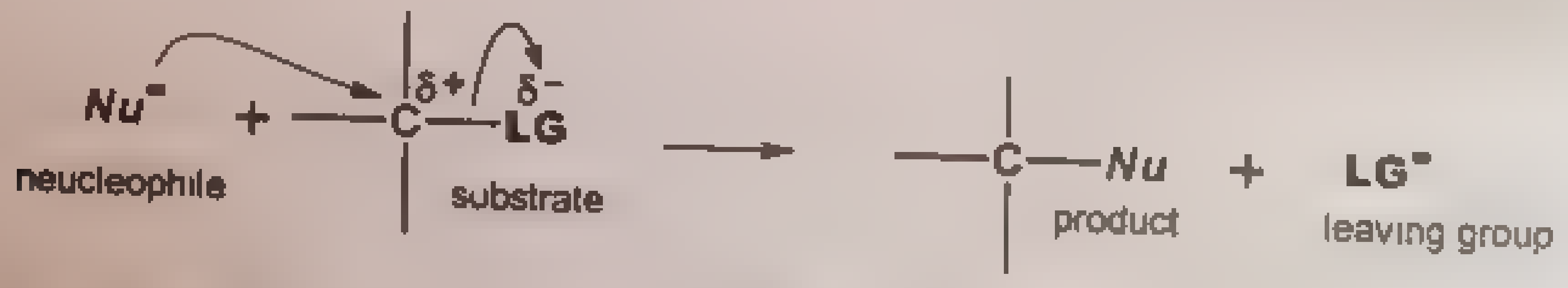
Substitution Reaction

A substitution is the reaction in which one group replaces another.

NUCLEOPHILIC SUBSTITUTION REACTION

The reaction in which a nucleophile replaces another atom or a group of atom already present molecule are called nucleophilic substitution reactions.

In these reactions, an electron rich species, the **nucleophile**, reacts at an electrophilic **C** atom attached electronegative group, the **leaving group**, which is replaced



- The electrophilic **C** is present in the polar sigma bond due to the presence of an electric substituent (**e.g., C-Cl, C-Br, C-I** and **C-O**)
- Nucleophilic substitution reactions allow the interconversion of functional groups

TYPES OF NUCLEOPHILIC SUBSTITUTION REACTION

There are two fundamental events in a nucleophilic substitution reaction

1. formation of the new σ–bond to the nucleophile
2. breaking of the σ–bond to the leaving group

Depending on the relative timing of these events, two different mechanisms are possible

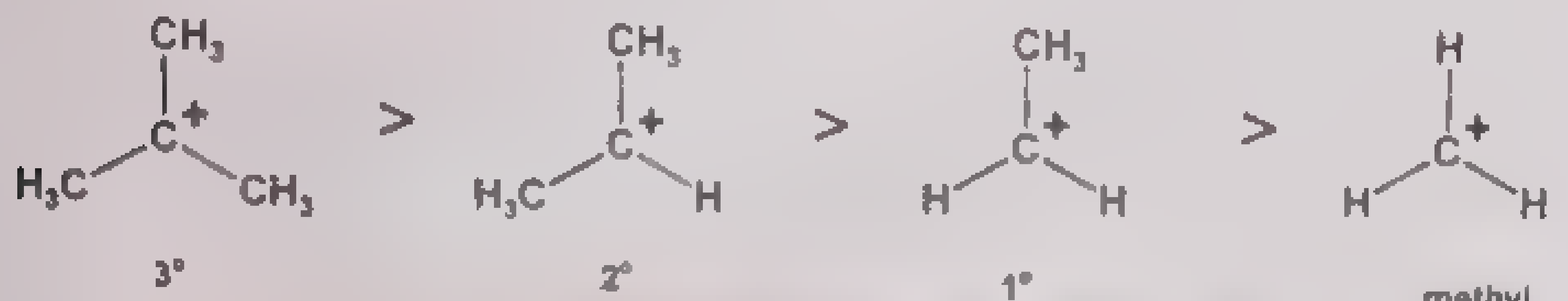
- First old bond breaks and then new bond is formed — ***S_N1 reaction***
- Simultaneous bond formation and bond breaking — ***S_N2 reaction***

CARBOCATIONS AND THEIR STABILITY

The ion with trivalent carbon and have positive charge on carbon atom is called a carbocation

Stability:

- The general stability order of simple alkyl carbocations is ***(most stable)*** 3° > 2° > 1° > methyl ***(least stable)***



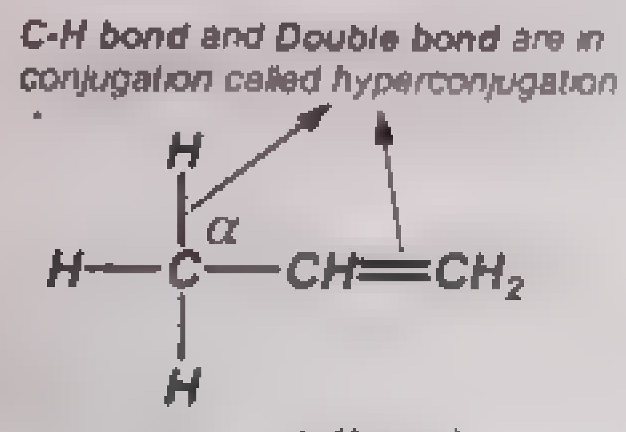
- This is because alkyl groups are weak electron donating due to hyperconjugation and inductive effects. So, due to electron donating effect, they stabilize the positive charge on carbon atom
- Since, tertiary carbocation has more alkyl groups attached to the positive carbon atom, so, it will be more stabilized than secondary carbocation and so on
- Resonance effects can further stabilize carbocations when present. *For Resonance Effect see page 215*

SOME EXPLANATIONS

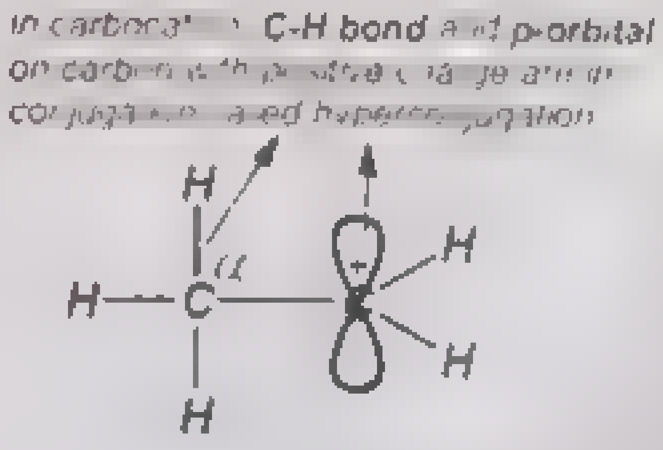
Hyperconjugation

The conjugation of σ – electrons of a C – H bond with p – electrons of the unsaturated system or with p – orbital is called hyperconjugation.

Examples:



(alkene)



(carbocation)

Inductive Effect

The polarization of a bond induced by an adjacent polar bond is known as the Inductive Effect

Example

$$\overset{\delta\delta^+}{\underset{2}{H_3C}} \rightarrow \overset{\delta^+}{\underset{1}{CH_2}} \twoheadrightarrow \overset{\delta^-}{Cl}$$

In ethyl chloride, the more electronegative chlorine atom pulls shared electron towards [illegible] charge and C-1 gets δ⁺ charge. The C-1 in turns pulls electrons from C-2. Thus C-2 also gets slight δδ⁺ charge. However, charge on C-2 is less than C-1 because pull decreases along the chain

REACTIONS INVOLVING CARBOCATIONS

NUCLEOPHILES AND BASE

It is species rich in electron and has an unshared pair of electrons available for bonding

-
-

Examples

... is a species rich in electron attacks on carbon atom, then it is a nucleophile; ... hydrogen atom then it is called a base.

$HO^- + CH_3\text{—}CH_2\text{—}Br \longrightarrow CH_3\text{—}CH_2\text{—}OH + Br^-$

Nucleophile

$HO^- + CH_2(H)\text{—}\overset{\delta+}{C}H_2\text{—}\overset{\delta-}{Br} \longrightarrow CH_2\text{=}CH_2 + H_2O + Br^-$

Base

SUBSTRATE AND LEAVING GROUP

SUBSTRATE MOLECULE

The alkyl halide molecule on which a nucleophile attacks is called substrate molecule

LEAVING GROUP (LG)

Leaving group is also a nucleophile. It leaves with an unshared pair of electrons

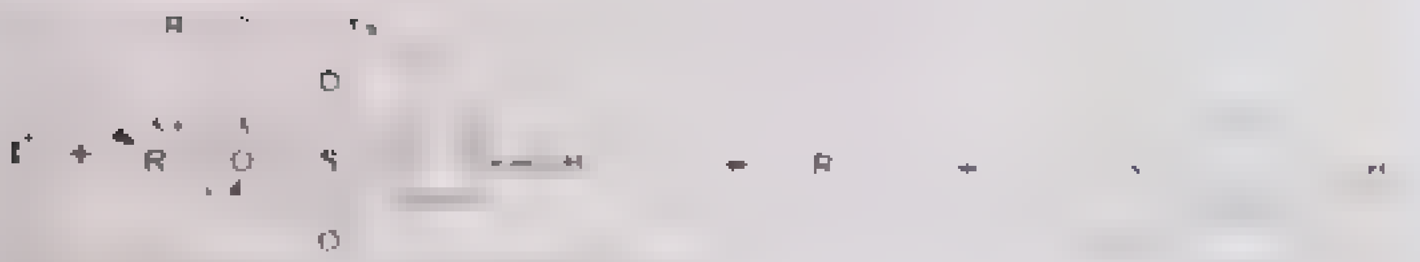
- The incoming nucleophile ...
- Good Leaving Groups are ...
- Poor leaving groups are ...
- Iodide ion is a good nucleophile ... a good leaving group

$$H\text{—}A \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$$

acidic – the more H^+ the more acidic

Both these process are similar as both involves ionization

- The first reaction represents the Bronsted acid dissociation.
- The second reaction represents the loss of a leaving group in an S_N1 type reaction



Alkyl p-toluenesulphonate or Alkyl tosylate or ROTs

Exercise Q3 (ii). Explain in detail S_N1 and S_N2 reactions with

S_N1 MECHANISM

It is substitution nucleophilic unimolecular

EXPLANATION

Step-I The

$$R-X \longrightarrow R^{+} + X^{-}$$

Step-II Then the carbocation

$$R^{+} + Nu^{-} \longrightarrow R-Nu$$

- Since only one molecule is

two step, unimolecular nucleophilic

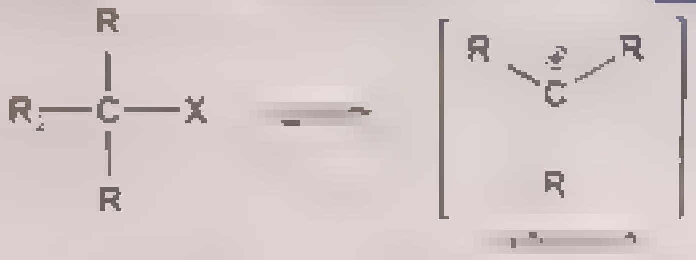
EVIDENCES OF S_N1 MECHANISM

1. Kinetic Evidence.

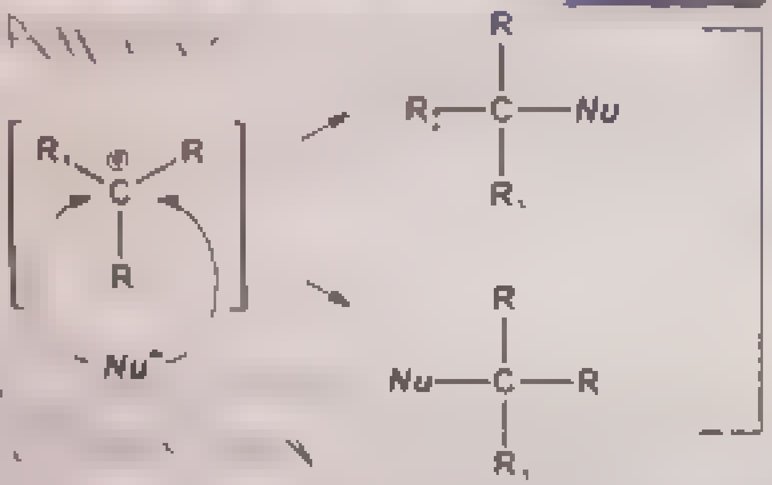
- The rate of an S_N1 reaction depends upon the concentration [illegible].
- The [illegible] concentration [illegible]. Thus
  Rate = k [RX]
- This is because the nucleophile [illegible] step. Hence the rate of reaction does not depend on the [illegible] nucleophile.

2. Stereochemical Evidence.

- Experiments have shown that [illegible].
- The extent of partial [illegible] stability of [illegible].



- The [illegible].
- The [illegible] carbon [illegible].

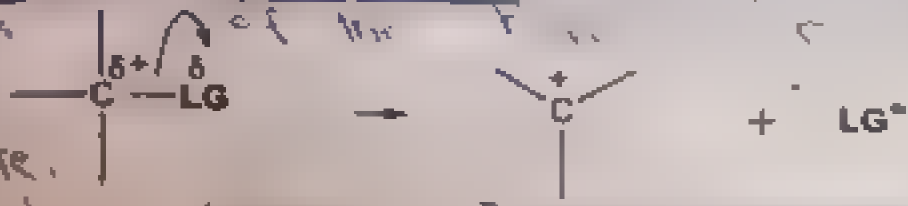


Atoms Pl.

Racemic Mixture

- ***However, Partial Racemization generally occurs during S_N1 reactions***
- ✓ Consider the case of unstable carbocation, the [illegible] group [illegible].
- ✓ Hence, the side of carbon atom to which the [illegible] of nucleophile
- ✓ Thus, the attack of nucleophile is greater from the side [illegible] of [illegible] leading inversion of configuration.
- ✓ Hence one enantiomer is formed in more amount, therefore the product has some optical [illegible].

Step 1. Slow loss of [illegible] generate intermediate.



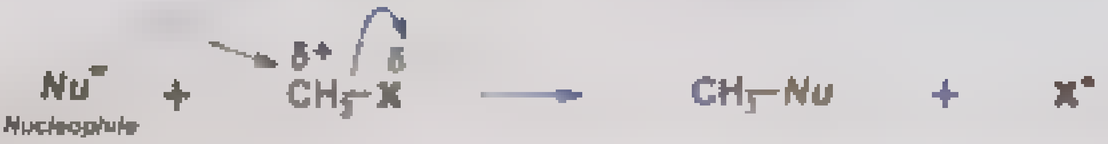
Step 2: Rapid attack [illegible]

electrophilic bond. carbocation

S_N2 MECHANISM

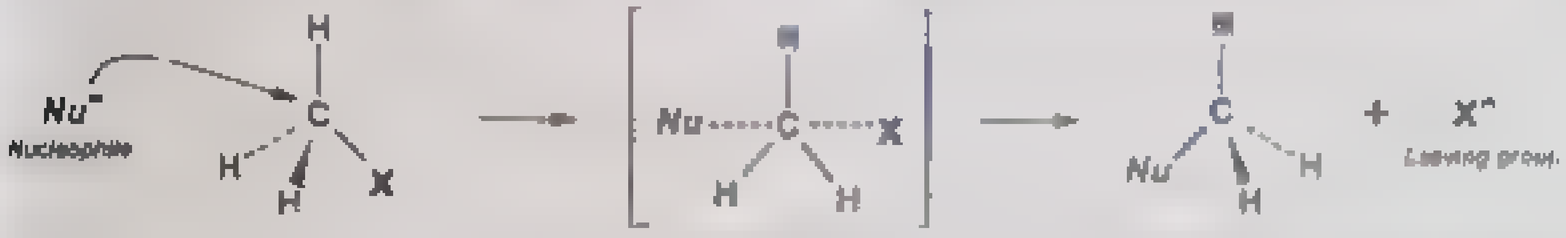
It is substitution nucleophilic bimolecular reaction. It occurs in one step.

Example



Mechanism

- The attack of nucleophile on carbon and the departure of ... single step



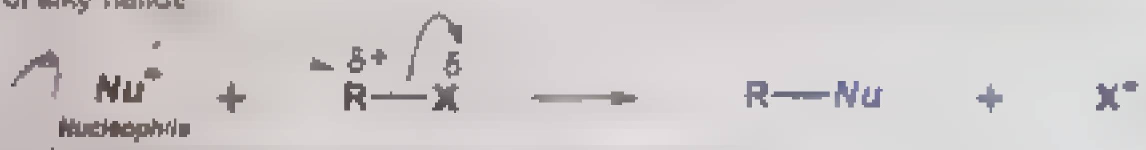
Transition State

- The reaction occurs in one step, so it is the rate determining step. In this one step ... and bond making processes occur simultaneously.
- Since two molecules a... bimolecular nucleophilic substitution reaction.

EVIDENCES FOR S_N2 MECHANIMS

(1) Kinetic Evidence

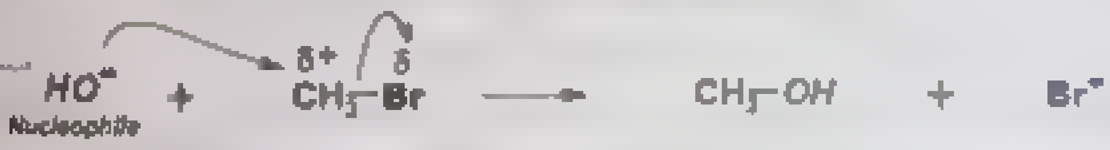
- The rate of an S_N2 reaction depends upon the concentration of ... of alkyl halide



The rate expression for the reaction can ...

Rate = K[Nu][R X] where K ...

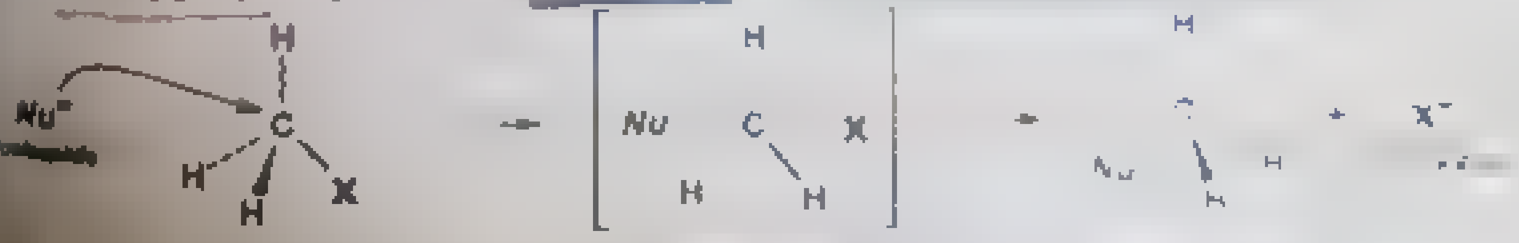
e.g.



- This means that the rate of ... e.g. the rate of following reaction increases if conc. of ...

(ii) Stereochemical Evidence

- A bimolecular nucleophilic substitution always occurs with inversion ...
- The carbon atom in transition state is sp ... leaving groups are present in the transition state on opposite ...



Transition State

COMPARISON OF S_N1 AND S_N2 MECHANISM

Sr. No.	S_N1	Sr. No.	S_N2
(1)	It is a two step mechanism	(1)	It is a single step mechanism [illegible]
(2)	First step is slow one and second is fast	(2)	It has [illegible]
(3)	It is a unimolecular reaction	(3)	It is a bimolecular reaction
(4)	It is favoured in polar solvents	(4)	It is [illegible]
(5)	Mostly tertiary alkyl halides give this reaction	(5)	Mostly primary alkyl [illegible]
(6)	50% inversion and 50% retention of configuration takes place	(6)	[illegible] configuration [illegible]
(7)	Rate = k [RX]	(7)	Rate = k [RX] [Nu]

Exercise Q3 (iv) What are β-elimination reactions? Explain them with detail

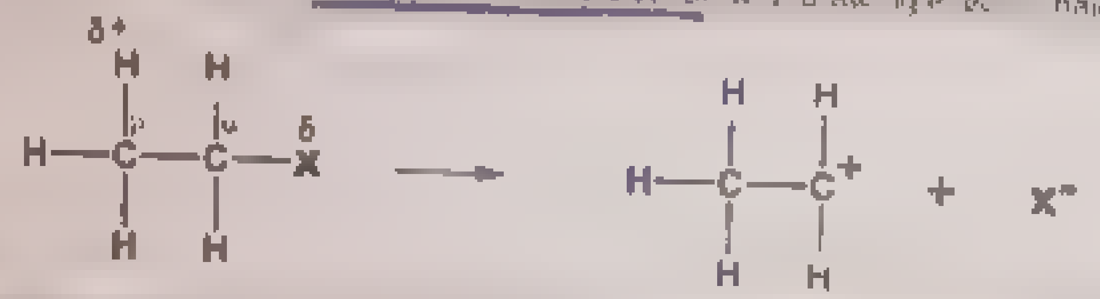
1,2-ELIMINATION REACTIONS (β-ELIMINATION REACTIONS)

The chemical reaction in which two groups are eliminated without being replaced from a molecule is elimination reaction. When β hydrogen is eliminated, it is called β-elimination reaction or 1,2-elimi-reaction

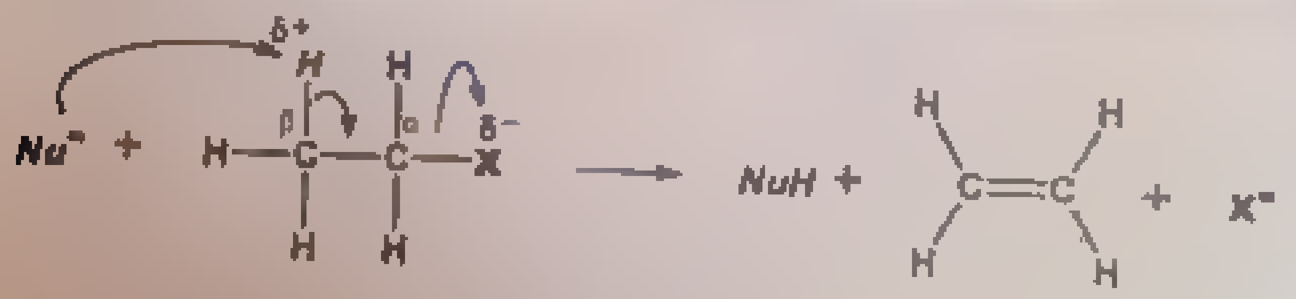
Explanation.

- β hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen [illegible]

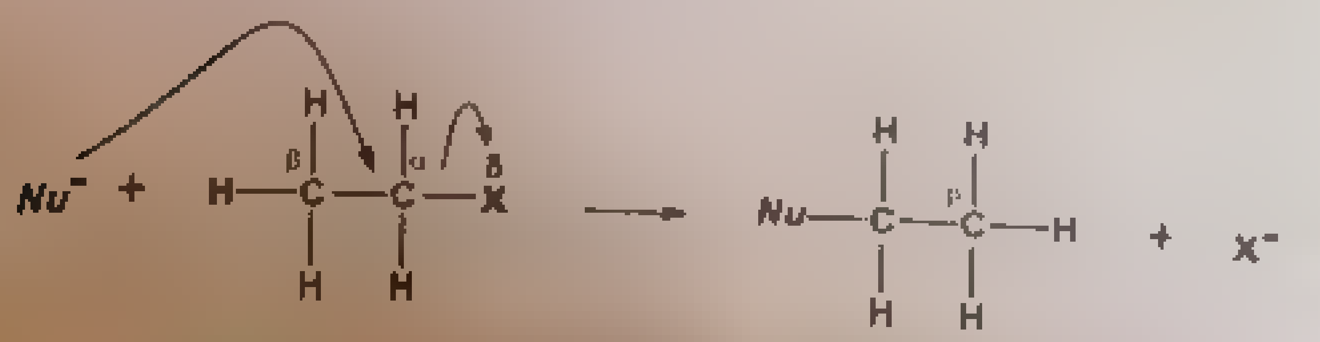
$CH_3CH_2^+$



- The attacking nucleophile can either attack α carbon to give S_N or it abstracts β proton to give β elimination reaction



(Elimination)



[illegible]

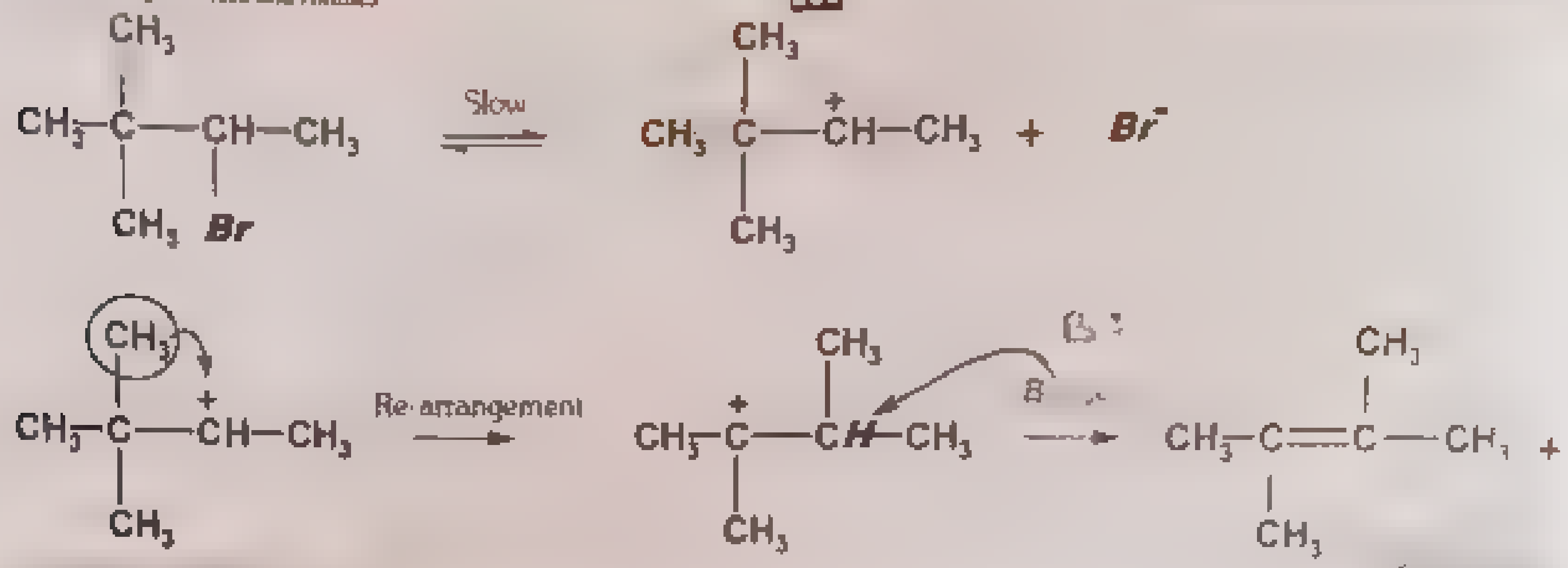
EVIDENCES [illegible]

1. [illegible]

[illegible]

2. [illegible]

[illegible]

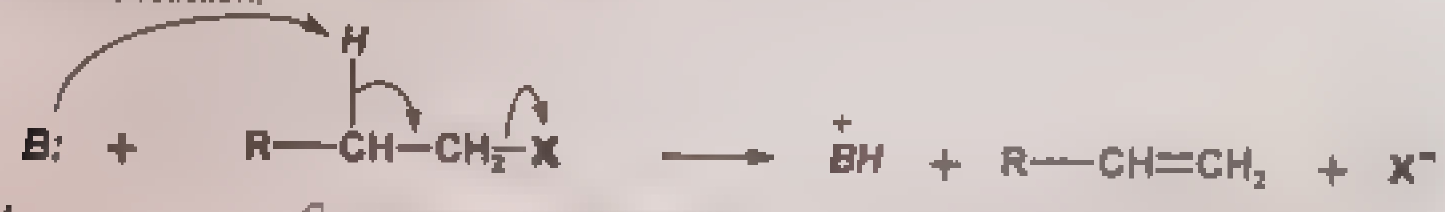


E2 MECHANISM

It is bimolecular one step elimination reaction

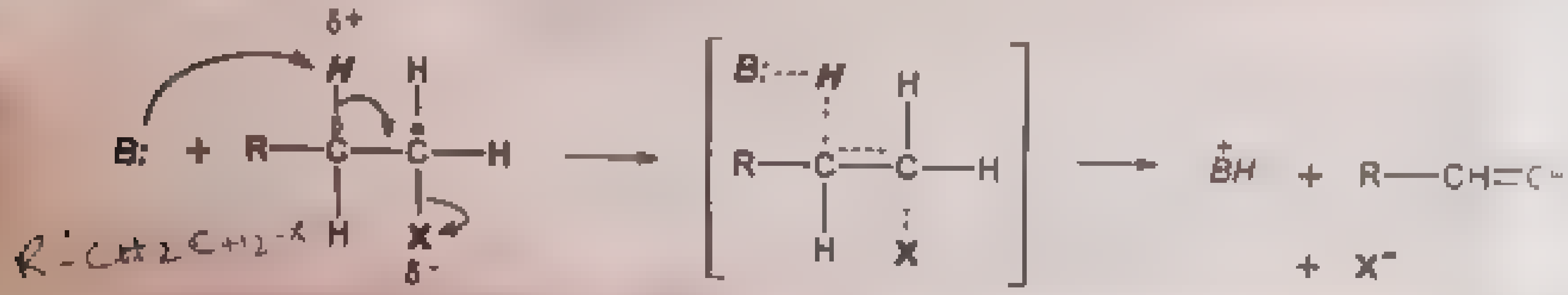
Example:

Consider the reaction,



Mechanism:

- It is a one-step reaction.
- The attacking base removes a proton from the β-carbon simultaneously with the formation of doub... between C_α and C_β and the loss of halide ions



- This is rate determining step because bond breaking and bond making processes are ... place sim...
- Since two molecules are undergoing a change in transition state it is a one step bimolecular ... reaction.

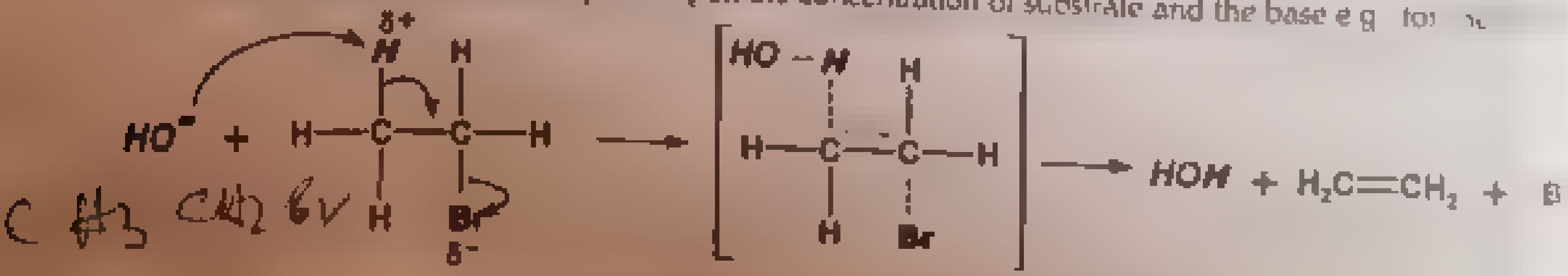
EVIDENCES FOR E2 MECHANISM

(1) Kinetic Evidence

- The E2 is a one-step process in which both the substrate and the base participate. Thus ... law of the E2-reaction is

Rate = k [Substrate][Base]

Thus, the rate of E2 reaction depends upon the concentration of substrate and the base e.g. for ...



The rate of reaction follows second order kinetics i.e. Rate = $k[CH_3CH_2Br][HO^-]$

SUBSTITUTION VERSUS ELIMINATION REACTIONS

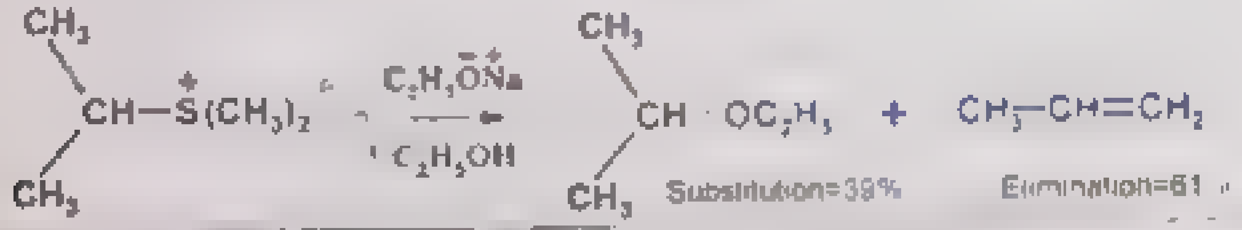
- The substitution and elimination reactions ... between them because ...
- Energetically substitution is more ... reaction in the substrate ... elimination ...
- Elimination occurs only ... beta hydrogen ... H ... require this condition.

Following factors help to compare these two paths ...

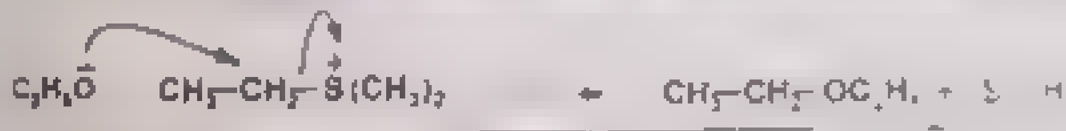
(i) Structure of Substrate:

Crowding within the substrate favors elimination over substitution.

It is because ... However the ... carbocation is easy.

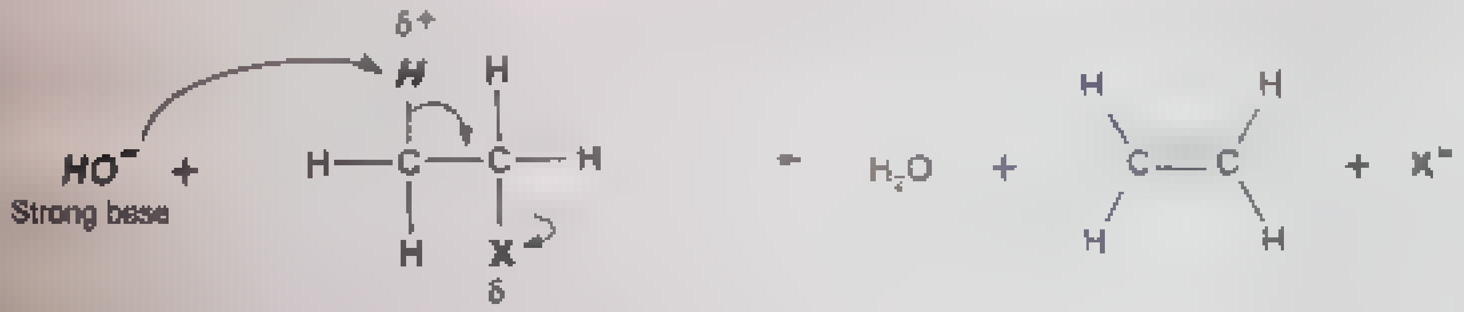


Remember:



(ii) Nature of Base:

- *When the electron pair donor is ... base e.g., HO⁻, RO⁻ etc. the dominant reaction is E2. The S_N2 reaction is a side reaction.*
- *However, when the nucleophile is a weak base ... the S_N2. The E2 will be a minor side reaction.*



CH_3-CH_2-X

(iii) The nature of Leaving Group:

- The ... reactions ... substitution reactions ...
- ... the better leaving group ... step ...
- However ... depends upon the ... group e.g. consider the following bimolecular ...

$$n\text{-}C_{16}H_{33}-CH_2-CH_2-X + (CH_3)_3COK \xrightarrow{(CH_3)_3COH} n\text{-}C_{16}H_{33}-CH=CH_2 + n\text{-}C_{16}H_{33}-CH_2-CH_2-OC(CH_3)_3$$

X = Br	85%	15%
X = OTs	1%	99%

Remember

OTs ... see page 230.

(iv) Nature of Solvent:

- ... while ...
- E1 is ... polar solvent ...
- In non polar solvents, the reaction will follow ...

(v) Effect of Temperature:

An increase in temperature will favor more than substitution.

It is because ... e.g.

$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + NaOH \longrightarrow CH_3-CH=CH_2 + CH_3-CH_2-CH_2-OH$$

At 45°C	53%	47%
At 100°C	64%	36%

QUICK QUIZ (1)

(1) What are monohaloalkanes

Monohaloalkanes are called alkyl halides. These have general formula R–X.
These may classified as primary, secondary or tertiary alkyl halides.

(2) What are primary, secondary and tertiary carbons atoms

- *A primary C-atom is attached to one or no carbon atom is called primary C-atom.*

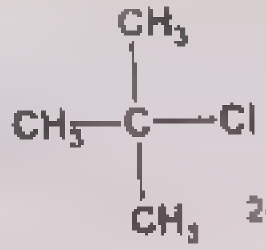
e.g. CH_3-Cl (Methyl chloride) CH_3-CH_2-Cl (Ethyl chloride)

- *A Secondary C-atom is attached to two C-atoms simultaneously ...*

e.g. $(CH_3)_2CH-Cl$ 2-Chloropropane $CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-CH_3$ 2-Chlorobutane

- A tertiary C-atom is attached to three C-atoms simultaneously is called a tertiary C-atom

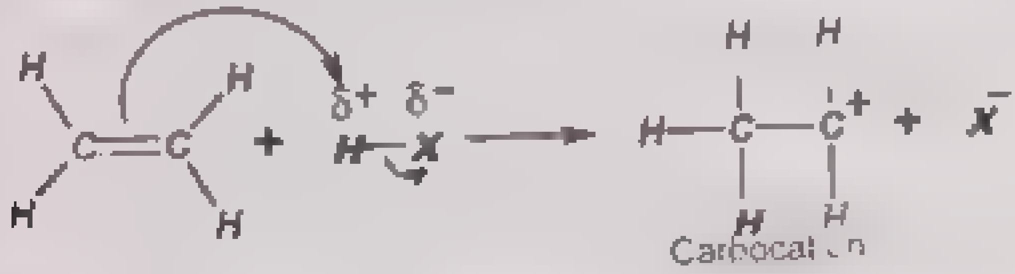
e.g.



2-Chloro-2-methylpropane

3) What is carbonium ion

A carbocation is a reaction intermediate. It is trivalent with a positive charge on carbon atom. It can be produced as follows



NOTE. Carbonium ion is an old term. It is no longer in use. The current term for such species is carbocation.

(4) What is leaving group

Leaving group is a nucleophile that leaves during substitution reaction with an unshared pair of electrons.

- The incoming nucleophile must be stronger than the leaving group
- Good Leaving Groups are: Cl^-, Br^-, I^-, HSO_4^-
- Poor leaving groups are OH^-, OR and NH_2^-
- Iodide ion is a good nucleophile as well as a good leaving group

(5) What is sp^3-hybridization

The process of mixing one s orbital and three p orbitals to form four equivalent sp^3 hybrid orbitals is called sp^3 hybridization.

The ratio of s and p character in each sp^3 hybrid orbital is 1:3. Each sp^3 hybrid orbital has 25% s-character and 75% p-character.

e.g. In CH_4, carbon atom undergoes sp^3 hybridization

(6) Define bond polarity

The property of shared pair of electrons being attracted by one atom more than the other is called bond polarity.

e.g. the bond between H and Cl in HCl is a polar bond

(7) Define bond energy

The amount of energy required to break one mole of bonds ... is called bond energy.

e.g. $H_2 \rightarrow 2H$ $\Delta H = 435$ kJ/mol. Thus bond energy of H–H bond is 435 kJ/mol.

(8) What is a nucleophile?

A Species in search of positive charge is called a nucleophile ...

Or It is species rich in electron and has an unshared pair of electrons ...

It may be negatively charged or neutral.

Examples

HO^-	Hydroxide ion	H_2O	Water
$C_2H_5O^-$	Ethoxide ion		

$$A + B \longrightarrow A - B$$
$$A + B \longrightarrow A - B$$

ORGANOMETALLIC COMPOUNDS (GRIGNARD'S REAGENTS)

[illegible] and reactions of Grignard's reagent

Preparation of Grignard's Reagent

Procedure

- [illegible] of [illegible]
- [illegible]

$$\overset{\delta+}{R}-\overset{\delta-}{X} + Mg \xrightarrow{\text{ether}} \overset{\delta-}{R}-\overset{\delta+}{Mg}-X$$

$$CH_3-Br + Mg \xrightarrow{\text{ether}} CH_3-Mg-Br$$

[illegible] magnesium bromide

Important

- Alkyl bromides [illegible] used [illegible] the preparation of Grignard's reagents because of its intermediate [illegible]
- When more [illegible] halides are used the high [illegible] solvent such as tetrahydrofuran is employed [illegible] because reflux
- When less reactive [illegible] halides are used
- Alkyl magnesium [illegible] are not isolated but are used as ethereal layers

REACTIVITY

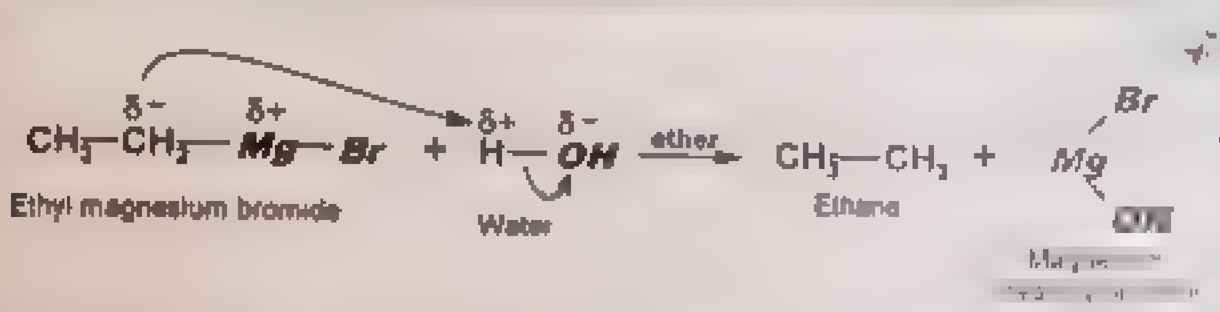
- Organometallic compounds are nucleophilic because of partial nega...

$$\overset{\delta-}{R} - \overset{\delta+}{Li}, \qquad \overset{\delta-}{R} - \overset{\delta+}{Mg} \quad X$$

- Carbon atom being more electronegative than metals such as Mg, Li etc. ... partial negative charge. Thus organometallic compounds act as source of ...

$$\overset{\delta-}{CH_3} - \overset{\delta+}{Mg} - \overset{\delta-}{Br}, \qquad CH_3 - \overset{\delta+}{Li}$$

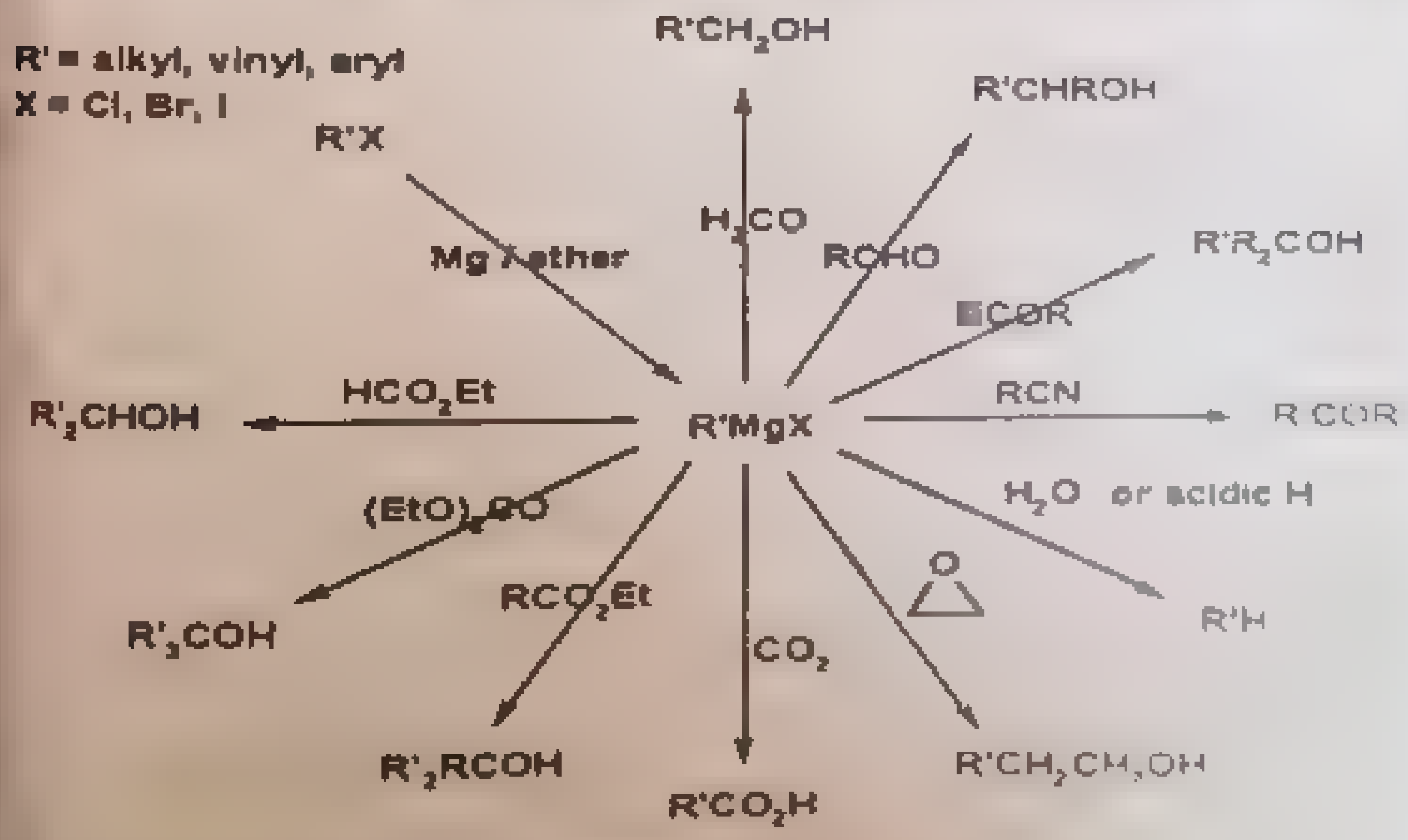
- The following reaction supports the nucleophilic character of organo...



Remember! *Abbreviations for common Alkyl/Aryl groups. These are to be used ... Methyl (Me), Ethyl (Et), n Propyl (n-Pr), isopropyl (iso-Pr), Phenyl (Ph) ...*

REACTIONS OF GRIGNARD'S REAGENTS

Brief Summary



Typical work-up for these reactions:
1. Dilute aqueous acid or
2. Aqueous ammonium chloride

(1) With Aldehydes and Ketones

This is done to produce primary, secondary and tertiary alcohols.

These reactions are carried in the presence of ether followed by acidic hydrolysis

Classification of Monhydric Alcohols

The alcohols containing only one hydroxyl group (OH) are called monohydric alcohols.

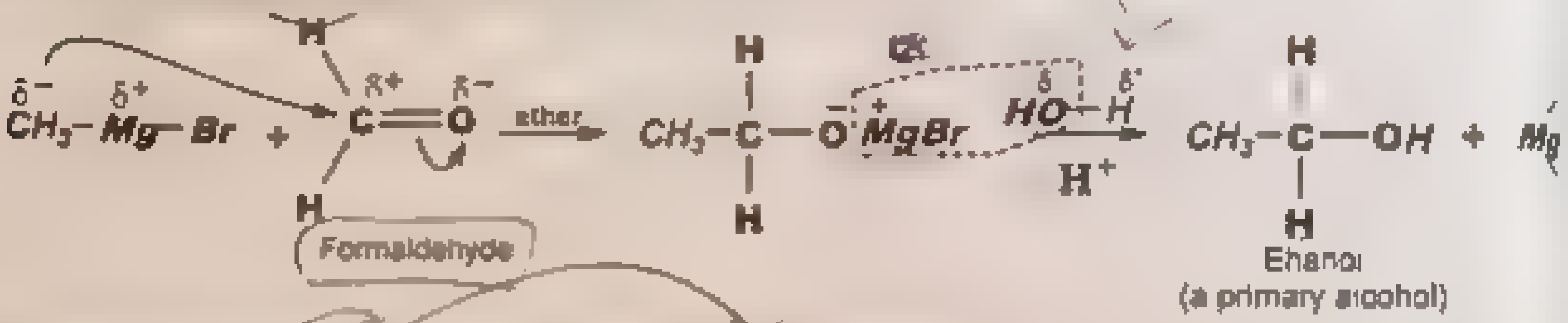
Monohydric alcohols are classified into the three types.

(i) Primary alcohols

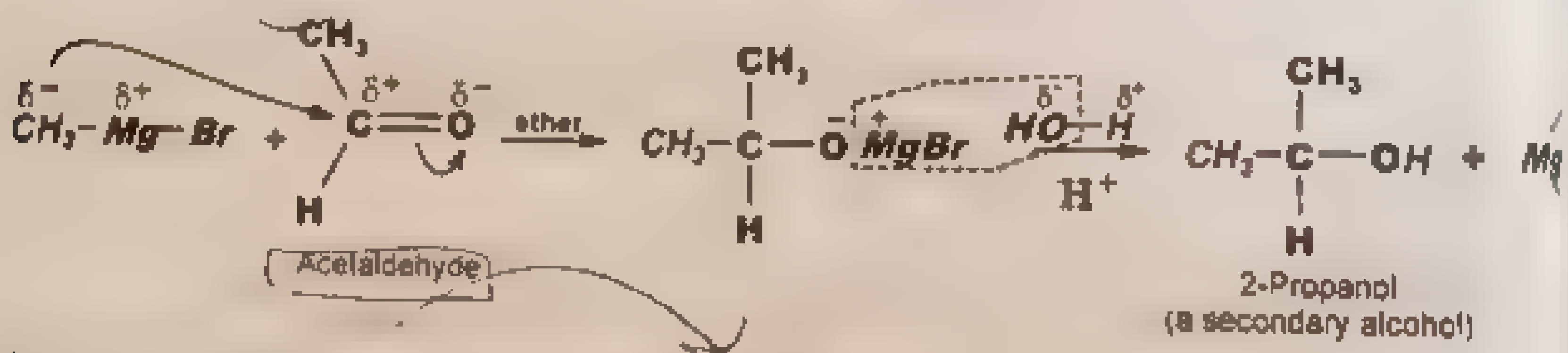
(ii) Secondary alcohols

(iii) Tertiary alcohols

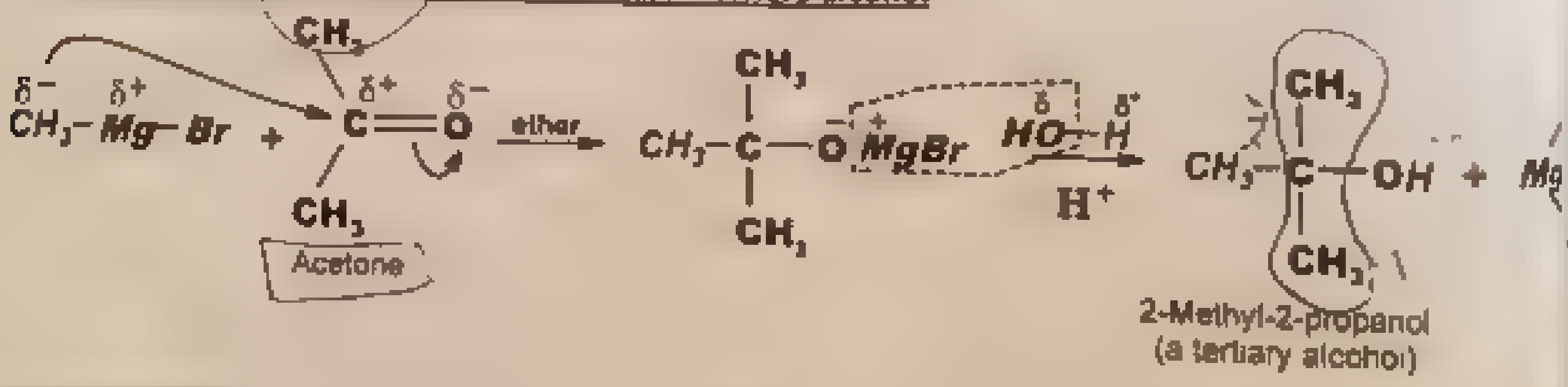
(i) Reaction with Methanal (Aldehyde) to form primary alcohol



(ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol



(iii) Reaction with Propanone (Ketone) to form tertiary alcohol



(2) With Esters

- Carboxylic esters, R_1COOR_2 react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- The tertiary alcohol contains 2 identical alkyl groups which comes from two units of Grignard reagent.
- The reaction proceeds via a ketone intermediate. It further reacts with the second equivalent of organometallic reagent to give tertiary alcohol.
- Since the ketone is more reactive than the ester, the reaction cannot be stopped at the ketone stage. Hence this reaction cannot be used for the preparation of ketones.

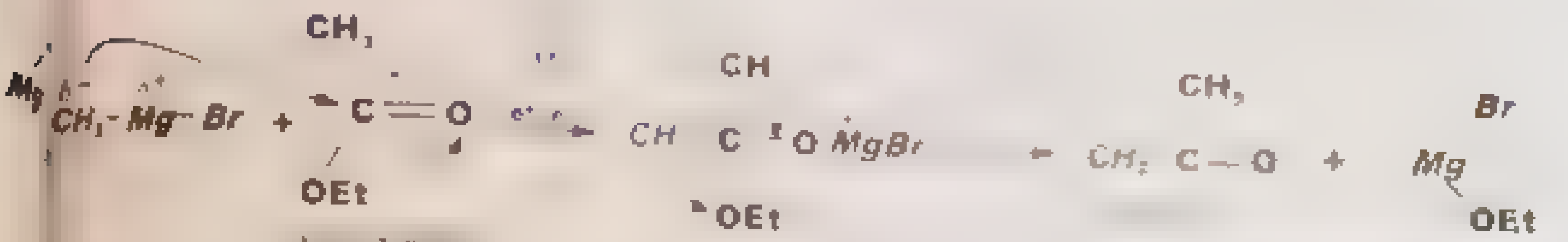
The Reaction type is Nucleophilic Acyl Substitution

Step 1:

The nucleophilic ... the ester. Electrons from the C=O move to the ... complex

Step 2

The ... product ...

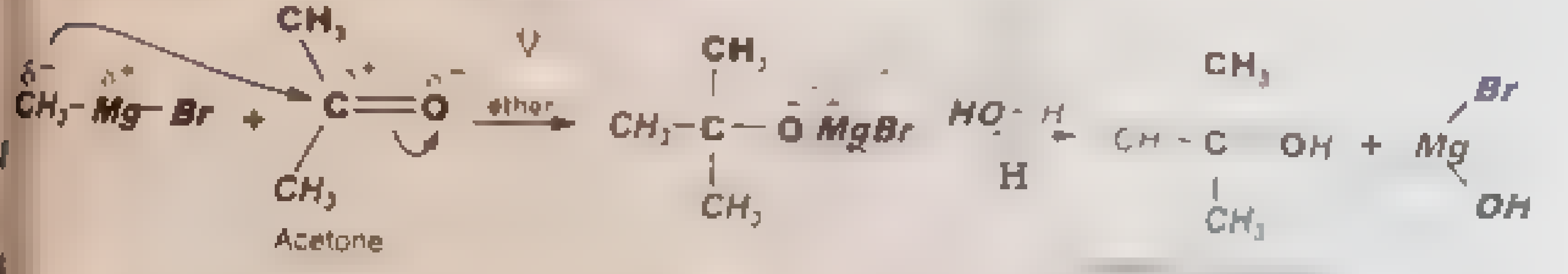


Step 3.

The nucleophilic C in the ... the ketone. Electrons from the C=O move to the ... complex

Step 4

This is the work up step ... alcohol product from the intermediate complex



QUICK QUIZ-2 (4) How does R-Mg-X reacts with CO_2

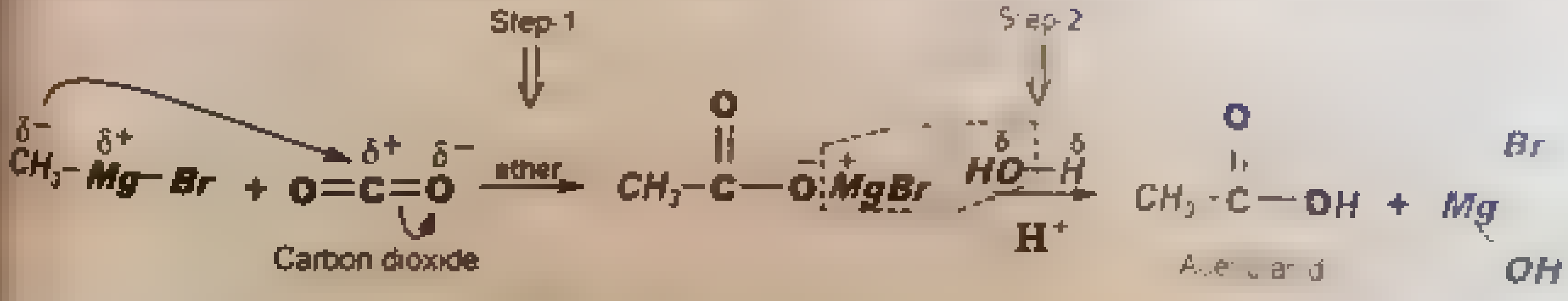
(3) With CO_2 (Carbonation of Grignard Reagents, RMgX)

Step 1

The nucleophilic C in the Grignard reagent adds to the elect... from the C=O move to the electronegative O creating an intermediate ...

Step 2:

This is the work-up step. It is a simple acid base reaction. Produ... carboxylic acid product from the intermediate complex



QUICK QUIZ-2

(1) What are Organometallic Compounds?

The compounds containing at least one bond between carbon atom of organic compound and metal atom are called organometallic compounds

Examples: Grignard's reagent, e.g. $H_3C-Mg-Cl$ Alkyl Lithium compounds, e.g. H_3C-Li

(2) Define protonation

The addition of a proton (H^+) to an atom, molecule, or an ion, forming its conjugate acid is called protonation

Example

(3) What is formula of Organolithium?

The general formula of organolithium compounds is R-Li, where R is an alkyl group or Ar-Li where Ar is aromatic group.

Examples: Methyl lithium, H_3C-Li Phenyl lithium, $Ph-Li$

(4) How does R-Mg-X reacts with CO_2

Solved on Page 232 above

(5) Write the formula of Grignard's reagent

The general formula of Grignard's reagent is R-Mg-X where R is an alkyl group and X is a halogen atom

Examples. Methyl magnesium chloride $H_3C-Mg-Cl$ Ethyl magnesium bromide $H_3C-CH_2-Mg-Br$

AMINES

Exercise Q3 (vii) What are the amines? Give its nomenclature.

The organic compounds containing NH_2 functional groups are called amines.

NOMENCLATURE

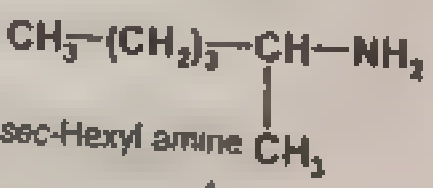
1. Common System of Naming

Aliphatic Amines

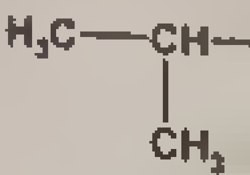
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals

$CH_3-CH_2-NH_2$

Ethyl amine

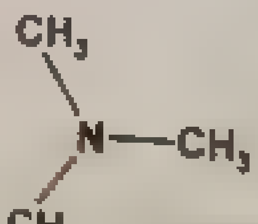


sec-Hexyl amine



Isohexyl amine

Dimethyl amine
(a secondary amine)

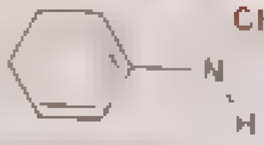


Trimethyl amine
(a tertiary amine)

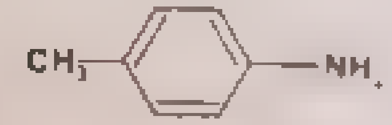
Aromatic Amines

Aniline $C_6H_5NH_2$ containing methyl gr... substituted in $-NH_2$ its name is represent... N-atom and not on the ring ...

Pyridine



N-Methyl...



p-Toluidine

6. IUPAC System of Naming Amines

Primary amines

- Select the longest continuous carb...
- The amino group is indicated by a prefix amino followed by name of hydroca...
- Number the carbon atoms ...
- The position of amino grou...
- If more than one amino g...

CH_3-NH_2

Aminomethane

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H(NH_2)-\overset{1}{C}H_3$

2-Amino...

Secondary and Tertiary amines

- Secondary and tertiary amines are named by using a ... alkyl group except the largest alkyl group (e.g. dimethylamino, methylethylamino etc.)

$CH_3-CH_2-NH-CH_3$

Methylaminoethane

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-N(CH_3)_2$

1-Dimethylaminobutane

More Practice

Primary amines → 1-propan amine

1-prop ane 1-amine

$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-NH_2$

1-Amino propane

$\overset{3}{C}H_3-\overset{2}{C}(CH_3)(NH_2)-\overset{1}{C}H_3$

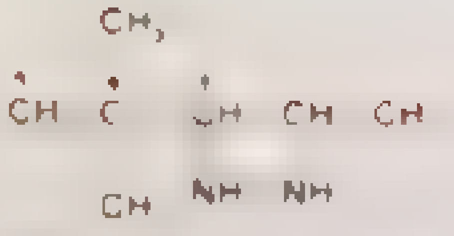
2-Amino-2-methylpropane

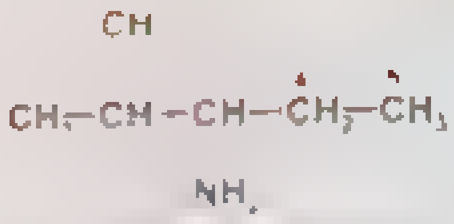
$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H(NH_2)-\overset{4}{C}H(CH_3)-\overset{5}{C}H_2-\overset{6}{C}H_3$

3-Amino-2,4-dimethylhexane

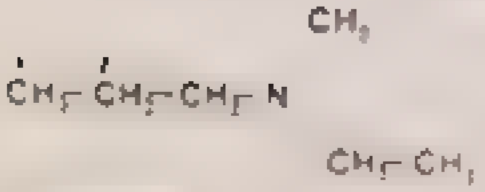
but ane 2-amine   2-butanamine

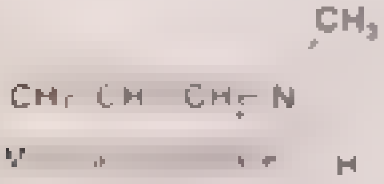
1° amine → because

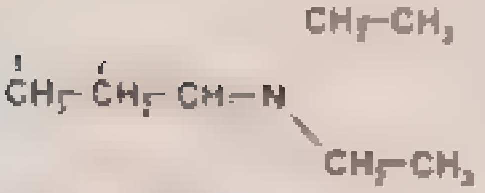


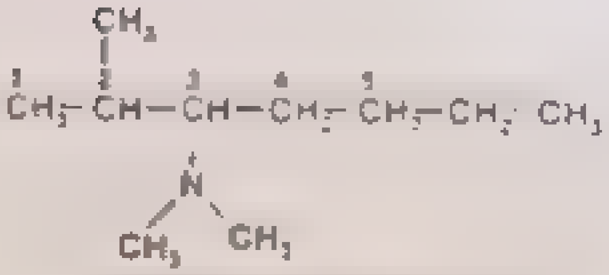


Secodary and Tertiary amines



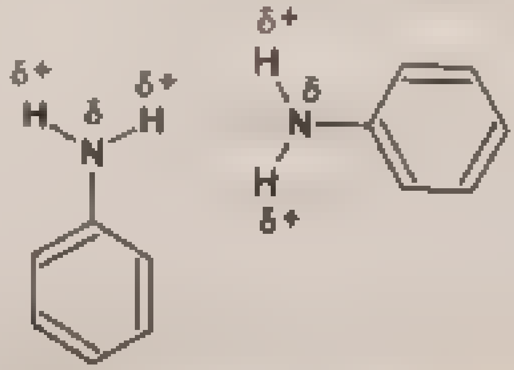






PHYSICAL PROPERTIES:

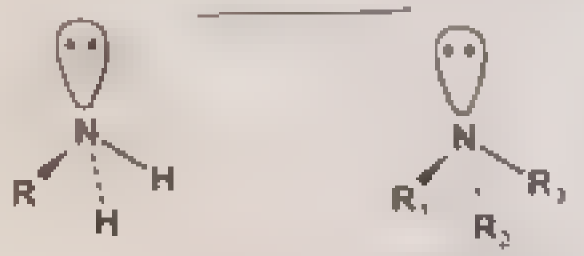
- The pola[illegible] difference of the two atoms, resu[illegible] formation [illegible] H-bonding systems (e.g. water
- Thus, amines have
  - high melting and boiling points compared to analogous alkanes
  - high solubility in aqueous media



Intermolecular hydrogen bonding in amines

STRUCTURE:

- In amines, nitrogen atom is sp^3 hybridised and has nearly tetrahedral structure.
- It forms three sigma bonds with its three sp^3-hybrid orbitals while the fourth non-bonding sp^3-hybrid carries a pair electron.

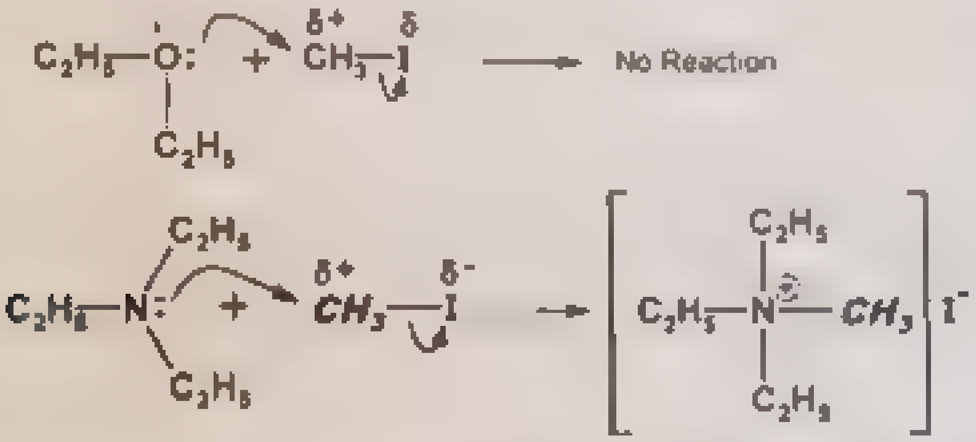


Optically active

- The non bonding electron pair is extremely important in explaining the chemical behaviour of amines. It is because it is responsible for the basic and nucleophilic properties of these compounds.
- An amine with three different groups is optically active.

BASICITY:

- Amines may act as bases towards acids and as Nucleophiles towards electrophile.
- They are more basic than alcohols and ethers and they are also more nucleophilic.
  e.g., ether does not react whereas at the same temperature amines gives addition product with CH_3I.



PREPARATION OF AMINES

(i) ALKYLATION OF AMMONIA BY ALKYL HALIDES

- The general reaction is

$$R—X + 2NH_3 \longrightarrow R—NH_2 + \overset{+}{N}H_4\overset{-}{X}$$

- When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of pri-, sec-, ter- amines and a quaternary ammonium salt is obtained.
- The reaction occurs with nucleophilic displacement of halide by ammonia or amines.

$$\ddot{N}H_3 + \overset{\delta+}{R}—\overset{\delta-}{X} \longrightarrow [R—NH_3]^+\overset{-}{X} \rightleftharpoons R—NH_2 + HX$$

- This reaction is further alkylation, e.g., accompanies by the following reactions

$$C_2H_5-I + NH_3 \longrightarrow \underset{\text{Ethyl amine (a primary amine)}}{C_2H_5-NH_2} + HI$$

$$C_2H_5-I + C_2H_5-NH_2 \longrightarrow \underset{\text{Diethyl amine (a secondary amine)}}{C_2H_5-NH-C_2H_5} + HI$$

$$C_2H_5-I + C_2H_5-NH-C_2H_5 \longrightarrow \underset{\text{Triethyl amine (a tertiary amine)}}{(C_2H_5)_3N} + HI$$

$$C_2H_5-I + (C_2H_5)_3N \longrightarrow \underset{\text{Quaternary ethyl ammonium iodide (a salt)}}{[(C_2H_5)_4N]^+ I^-}$$

- At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts, the quaternary salt is unaffected.
- The three amines are separated by fractional distillation.
- Over alkylation can be avoided by using excess of ammonia but the yield is low.

(2) REDUCTIONS OF NITROGEN CONTAINING FUNCTIONAL GROUPS:

(i) REDUCTION OF NITRILES

- Reduction of alkyl or aryl nitriles gives primary amines.
- The reduction may be brought about by $LiAlH_4$, or sodium in ethanol.
- Catalytic hydrogenation with Rh Al_2O_3, Pt or Raney nickel may also be employed to get primary am

$$R-C\equiv N + 2H_2 \xrightarrow[\text{heat}]{Ni} R-CH_2-NH_2 \text{ or } R-CH_2-NH_2$$

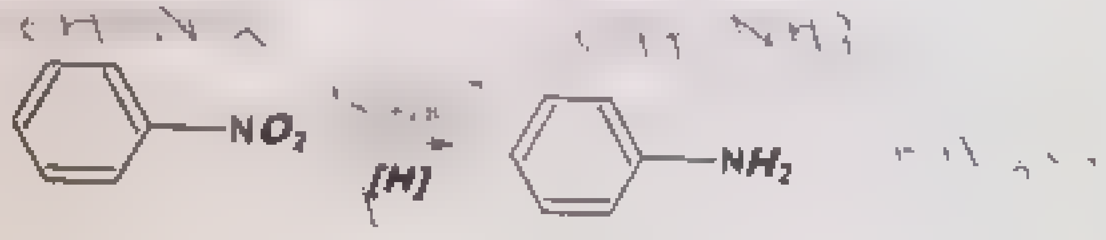
$$CH_3-CN + 2H_2 \xrightarrow{Rh, Al_2O_3} CH_3-CH_2-NH_2$$

(ii) REDUCTION OF NITRO COMPOUNDS

- The general reaction is

$$\underset{\text{Nitroarene}}{Ar{-}NO_2} \xrightarrow{[R]} \underset{\text{Primary aryl amine}}{Ar{-}NH_2}$$

- Nitroarenes can be reduced to primary aryl amines
- Typical reducing agents include Fe [illegible] Pd
- Nitro compounds on catalytic or chemical [illegible]

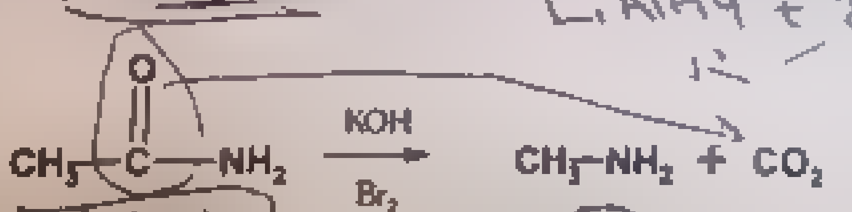


4-Nitroaniline

(iii) REDUCTION OF AMIDES

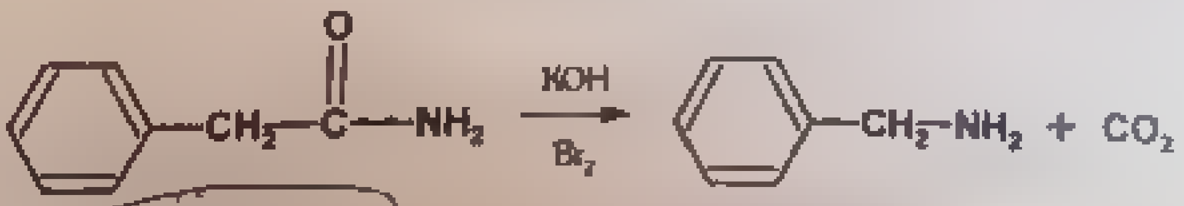
- The amides can be reduce to amines by reducing agents

- An amide on treatment with Bromine in the presence of KOH yields primary amines
- The reaction occurs through rearrangement.



Acetamide

Pri—amies



2-Phenylacetamide

Benzyl amine

Exercise Q 3 ix What are the main features which increase the basicity of amine?

REACTIVITY/BASICITY

- [illegible]
- [illegible]
  (i) [illegible]
  (ii) The rela[illegible]

  Consider the [illegible]

$$NH_3 + H^+ \rightleftharpoons \overset{+}{N}H_4$$

$$CH_3-NH_2 + H^+ \rightleftharpoons CH_3-\overset{+}{N}H_3$$

The strength of a base is expressed in terms of pK_b i.e

$$pK_b = -\log K_b$$

For ammonia and methyl amine the pK_b values are

$$pK_{NH_3} = 4.76 \quad ; \quad pK_{CH_3NH_2} = 3.38$$

Since $pK_{NH_3} < pK_{CH_3NH_2}$ methyl amine is a stronger base than ammonia.

It is due to two factors

(i) In ammonia, the lone pair of electron is attracted by 3 orbitals of hydrogen atoms. The CH_3 alkyl group has electron donating ability. Hence, in CH_3NH_2, sp^3 orbitals of carbon pushes electrons towards nitrogen. Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than ammonia.

(ii) The methyl ammonium ion ($CH_3NH_3^+$) is stabilized due to electron donating inductive effect of methyl group. On the other hand, NH_4^+ ion is not stabilized by hydrogen atoms since one pair on nitrogen has been used up.

Both these factors favor methylamine to a stronger base than ammonia.

- **Higher members show deviation from this behaviour**

  It is because the stabilization of a positive ion depends upon solvation, hydrogen bonding and resonance stabilization. Large size alkyl ammonium ions are less solvated. Also, large large size alkyl groups is highly non-polar so the solvation decreases in water.

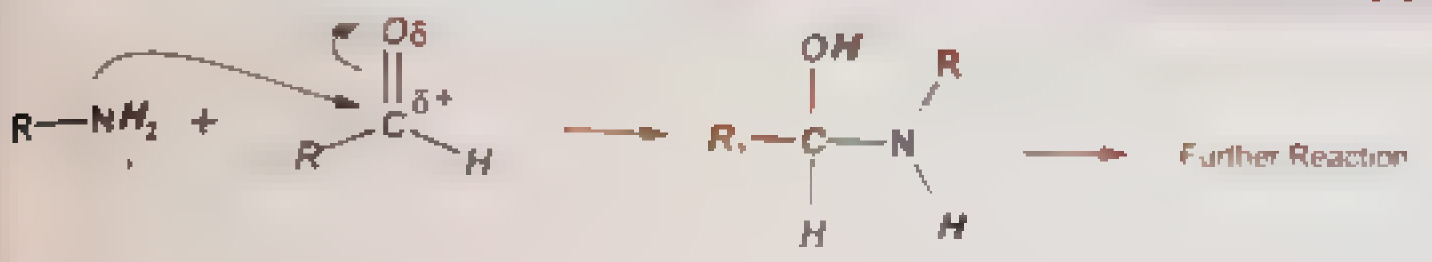
- Moreover, the availability of non bonding pair of electrons is also affected by steric factor [illegible] these aspects.

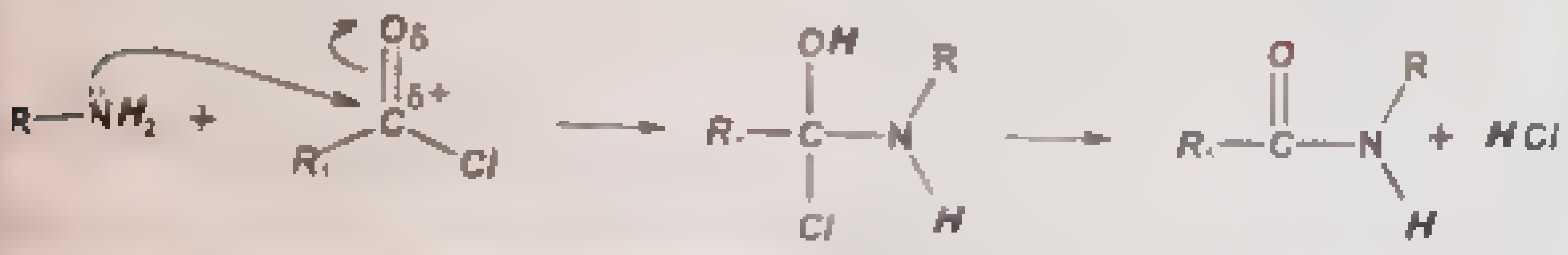
REACTIONS OF AMINES

The important organic reactions of amines (nucleophiles) are with the common electrophiles

- Alkyl halides via nucleophilic substitution
- Aldehydes or ketones via nucleophilic addition
- Carboxylic acid derivatives, especially acid chlorides or anhydrides via nucleophilic acyl substitution

$$R-NH_2 + \overset{\delta+}{R_1}-\overset{\delta-}{X} \longrightarrow R-\underset{\substack{|\\R_1}}{NH} + HX$$



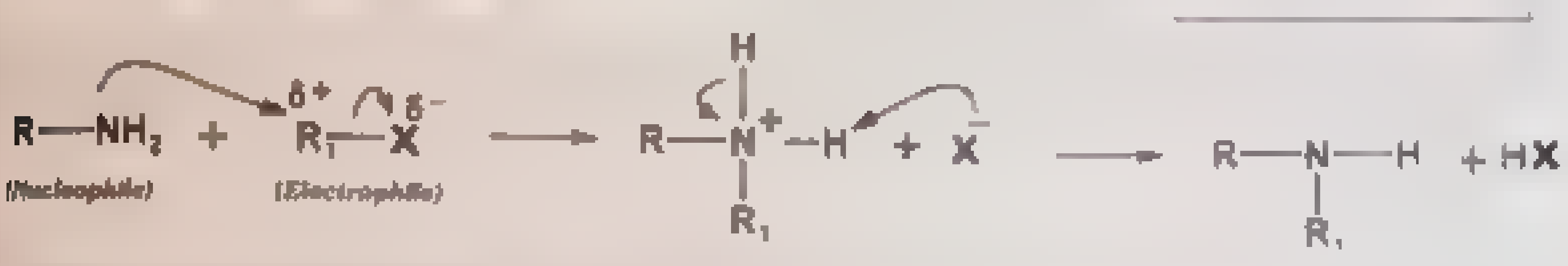


(i) ALKYLATION OF AMINE BY ALKYL HALIDES

The alkylation of amines is called alkylation

It produces secondary or tertiary amines

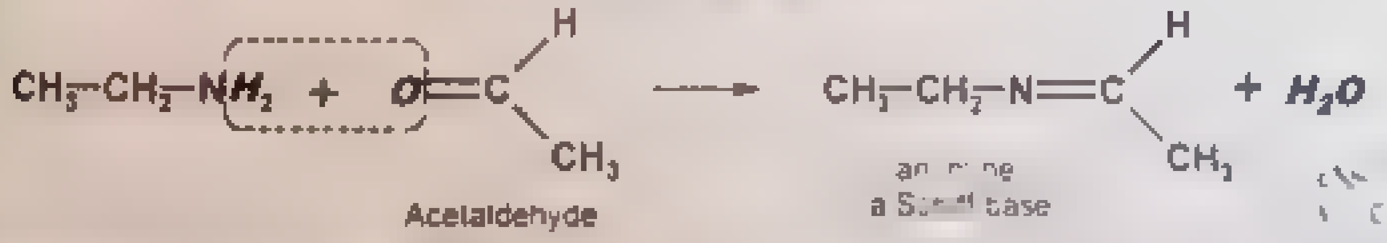
Same Reaction as on page 246



$R_1NH_3^+$ loses a proton with a base to give a free amine

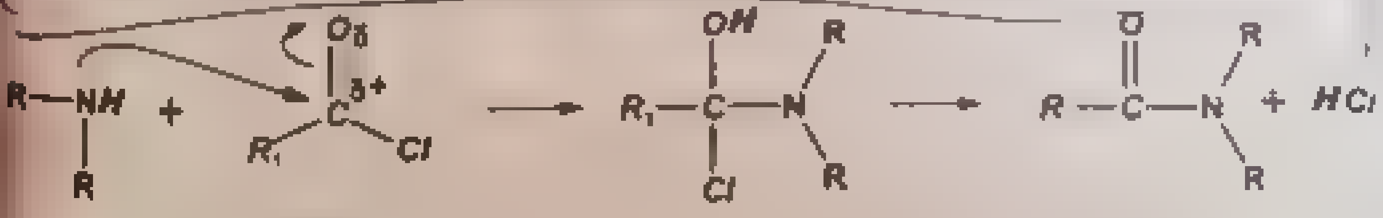
(ii) REACTIONS OF PRIMARY AMINES WITH ALDEHYDES AND KETONES

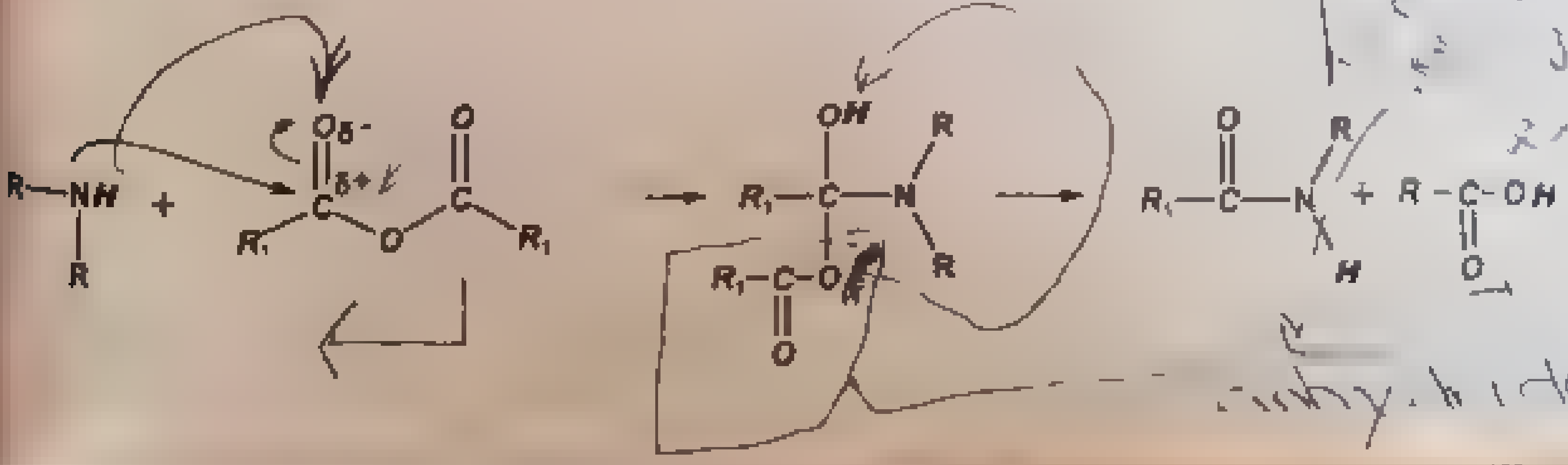
Aldehydes and ketones react with primary amines to form Schiff base



(iii) PREPARATION OF AMIDES

The amines react with acid halides and acid anhydrides to give amides





(e) PREPARATION OF DIAZONIUM SALTS

When amines react with ... as a ...

$$R-NH_2 + HNO_2 \longrightarrow R-\overset{+}{N}\equiv N + HO^- + H_2O$$

Diazonium ion

The diazonium group, group is rather unstable in the case of the ethyldiazonim ion it decomposes as

$$CH_3-CH_2-\overset{+}{N}\equiv N \longrightarrow N_2 + [CH_3-\overset{+}{C}H_2] \xrightarrow{H_2O} CH_3-CH_2-OH + H^+$$
$$[CH_3-\overset{+}{C}H_2] \longrightarrow CH_2=CH_2$$

When the group is attached to a benzene ring, through, the ion is stabilized to some extent by the ... electron of the ring. The benzenediazonium ... is therefore much more stable than its aliphatic co... Nevertheless, it decomposes readily above ...

QUICK QUIZ-3

(1) Define hydration

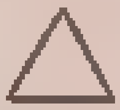
The addition of water to a substance is called hydration

Example: The addition of water to alkenes gives alcohols

(2) What is the difference between alicyclic and aromatic compounds

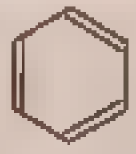
Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons

Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons

e.g. 

Cyclopropane

Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons

e.g. 

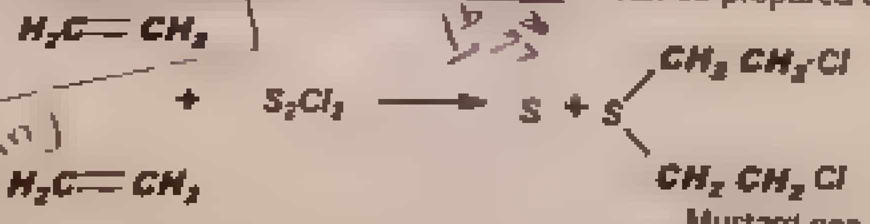
Benzene

(3) Define IUPAC

IUPAC stands for International Union of Pure and Applied Chemistry. The IUPAC is the accepted ... for chemical standards of nomenclature, measurements, and atomic mass values

(4) Write the equation for the preparation of mustard gas

Mustard gas is actually a high boiling liquid and has mustard like odour. It was used in World War ... it is a powerful vesicant, i.e. causes blisters. It can be prepared as follows



Mustard gas
(β,β'-Dichloroethyl sulphide)

(5) Define polymers

Polymerization is a process in which a small organic [illegible] combine together to form larger molecules. The substances [illegible]

e.g. *Polyethene, Polyvinyl chloride (PVC)*

(6) What is polymerization

Polymerization is a process in which a sma[illegible] ecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers

e.g.

$$n\ H_2C{=}CH_2 \xrightarrow[\text{traces of } O_2\ (0.1\%)]{100\ \text{atm}\ /\ 400°C} \left[\!-CH_2-CH_2-\!\right]_n$$

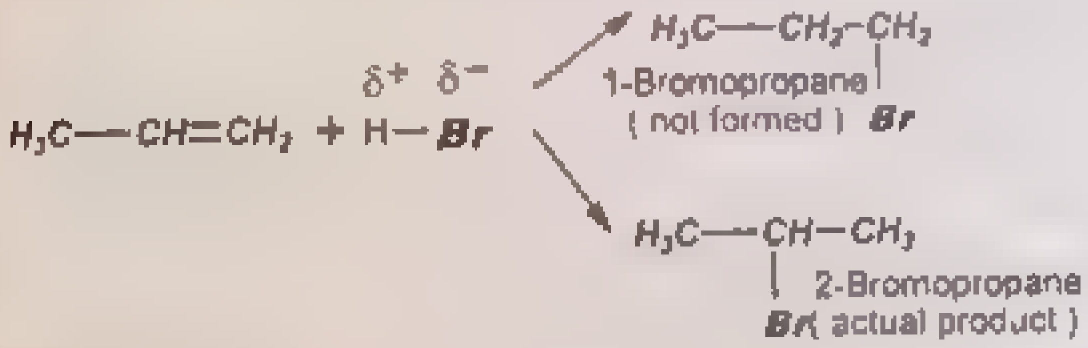
Ethylene → Polyethylene

(7) What is Markovnikov's rule?

It states

In the addition of an unsymmetrical reagent to [illegible] alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond which has least number of hydrogen atoms

Example:



(8) What are amines

The organic compounds containing $-NH_2$ functional groups are called amines

Examples:

$CH_3-CH_2-NH_2$

Ethyl amine

Aniline

(9) Why halogen of vinyl chloride is inert?

Halogen atom has one pair of electrons which come in resonance with the double bond of vinyl group

Thus the C to Cl bond develops some double bond character in it. Therefore it becomes very much difficult to displace this Cl atom by any nucleophile. Hence, the halogen atom of vinyl chloride is inert in substitution reactions.

Do You Know?

(i) CD's are made from vinyl chloride

(ii) Ethyl chloride is used as a typical anesthetic

(iii) Erupting volcanoes emit large quantities of halogens and halides

SOME IMPORTANT CONVERSIONS

(i) Ethyl bromide to propanoic acid

$$CH_3-CH_2-Br + Mg \xrightarrow{ether} CH_3-CH_2-Mg-Br$$

$$CH_3-CH_2-\overset{\delta-}{}Mg-Br + \underset{\text{Carbondioxide}}{O=C=O} \xrightarrow{ether} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O^{-}\overset{+}{M}gBr \xrightarrow[H^+]{HO-H} \underset{\text{Propanoic acid}}{CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH} + Mg\begin{matrix}Br\\OH\end{matrix}$$

(ii) Ethyl bromide to propane

$$CH_3-CH_2-Br + Mg \xrightarrow{ether} CH_3-CH_2-Mg-Br$$

$$CH_3-\overset{\delta-}{CH_2}-\overset{\delta+}{Mg}-Br + \overset{\delta+}{CH_3}-\overset{\delta-}{Br} \xrightarrow{ether} \underset{\text{Propane}}{CH_3-CH_2-CH_3} + Mg\begin{matrix}Br\\Br\end{matrix}$$

(iii) Ethyl bromide to Ethyl cyanide

$$CH_3-CH_2-Br + KCN \longrightarrow CH_3-CH_2-CN + KBr$$

(iv) Methyl bromide to Methyl alcohol

$$CH_3-Br + Mg \xrightarrow{ether} CH_3-Mg-Br$$

$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br + \underset{\text{Formaldehyde}}{H_2\overset{\delta+}{C}=\overset{\delta-}{O}} \xrightarrow{ether} CH_3-\overset{H}{\underset{H}{C}}-O^{-}\overset{+}{M}gBr \xrightarrow[H^+]{\overset{\delta+}{H}O-\overset{\delta-}{H}} \underset{\text{ethanol}}{CH_3-\overset{H}{\underset{H}{C}}-OH} + Mg\begin{matrix}Br\\OH\end{matrix}$$

Similarly secondary and tertiary alcohols can be prepared

(v) $CH_3CH_2CH_2Cl$ to $CH_3-CH=CH_2$

$$CH_3-\underset{H}{CH}-\underset{Cl}{CH_2} + KOH \xrightarrow{alcohol} \underset{\text{1-Propene}}{CH_3-CH=CH_2} + KCl + H_2O$$

(vi) CH_3-CH_2-Br to $(CH_3-CH_2)_4N\ Br$

$$NH_3 + \overset{\delta+}{CH_3}-CH_2-\overset{\delta-}{Br} \longrightarrow \underset{\text{Ethyl amine}}{CH_3-CH_2-NH_2} + HBr$$

$$H_3C-CH_2-NH_2 + \overset{\delta+}{CH_3}-CH_2-\overset{\delta-}{Br} \longrightarrow \underset{\text{Diethyl amine}}{(CH_3CH_2)_2NH} + HBr$$

$$(CH_3CH_2)_2NH + \overset{\delta+}{CH_3}-CH_2-\overset{\delta-}{Br} \longrightarrow \underset{\text{Triethyl amine}}{(CH_3CH_2)_3N} + HBr$$

$$(CH_3CH_2)_3N + \overset{\delta+}{CH_3}-CH_2-\overset{\delta-}{Br} \longrightarrow \underset{\text{Quaternary ethyl ammonium bromide}}{(CH_3CH_2)_4N^+Br^-}$$

SOCIETY, TECHNOLOGY AND SCIENCE

ORGANOMETALLIC COMPOUNDS IN MEDICINES

- *Cisplatin*
- *Arene* and *cyclopentadienyl complexes*
- *Mercurochrome (Merbromin)*
- *Merthiolate (Thiomersal)*
- *Salvarsan (arsphenamine in the States.*
- *Titanocene dichloride*, Cp_2TiCl_2
- *Tamoxifen* is an anticancer co...
- *Ferrocenyl* derivative chloroquine is a ...
- *Titanocene dichloride*, $(Cp)_2V(NCSe)_2$
- *Ferroquine* a combination of ferrocene a...
- *Vanadocene acetylacetonate* has poten...
- *Ru* $(\eta^6\text{-}C_6H_6)Cl_2(DMSO)$ has bee...

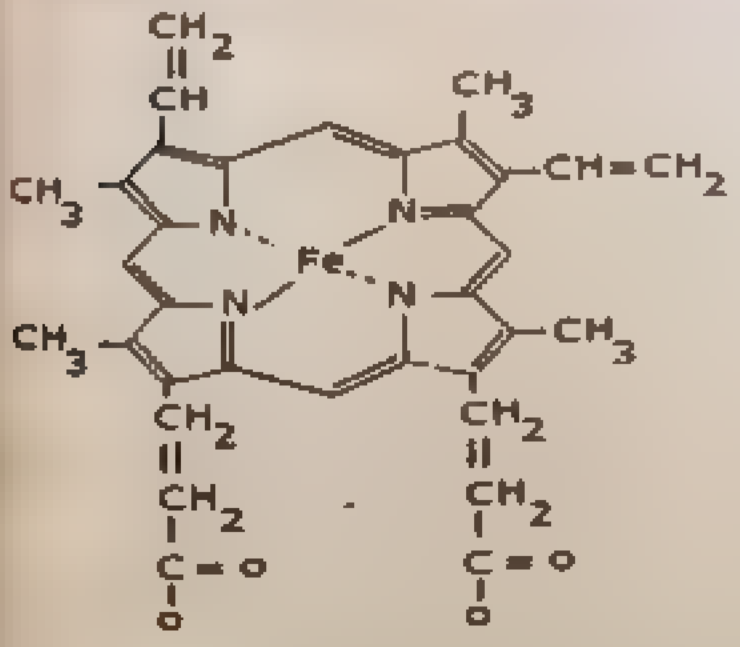
COMPARISON BETWEEN HEMOGLOBIN AND CHLOROPHYLL

Hemoglobin and chlorophyll both are ... porphyrin ring coordinated with a metal ion.

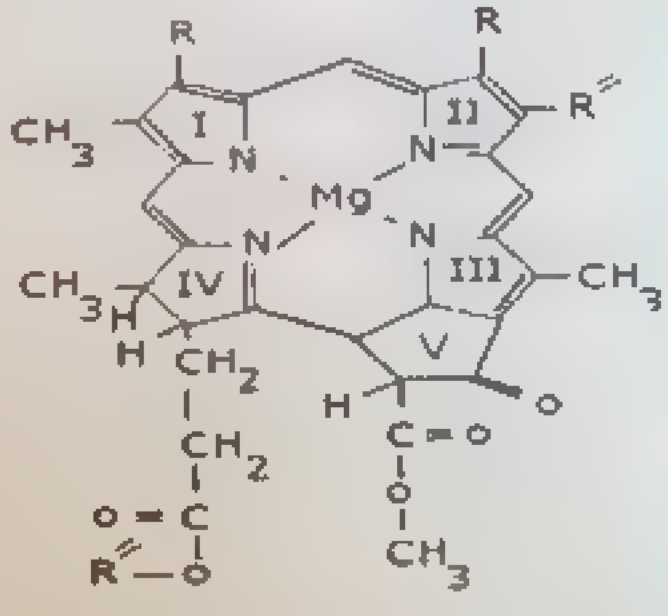
(1) Hemoglobin is a ...

(2) Hemoglobin is the red pigment in the blood, ... and certain organism.

(3) Hemoglobin is involved in oxygen transport ... photosynthesis.



Structure of Heme



Structure of Chlorophyll

KEY POINTS

- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- **Primary amines R-NH$_2$** or **ArNH$_2$** [illegible] aldehydes or ketones to give **carbinolamines** which then [illegible] **imines**
- **Primary alkyl or aryl amines** [illegible]

EXERCISE

Q1: Select the right answer from the choices given with each question.

(i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms:

(a) Two (b) Three (c) One (d) Four

(ii) S_N2 reactions can be best carried out with.

(a) Primary alkyl halides (b) Secondary Alkyl halides (c) Tertiary alkyl halides (d) All the three

(iii) For which mechanisms, the first step involved is the same:

(a) E_1 and E_2 (b) E_2 and SN_2 (c) E_1 and SN_2 (d) E_1 and SN_1

(iv) The rate of E_1 reaction depends upon,

(a) the concentration of substrate (b) the concentration of nucleophile

(c) the concentration of substrate as well as nucleophile (d) None of the above

(v) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because

(a) they have an electrophilic carbon

(b) they have an electrophilic carbon and a good leaving group

(c) they have an electrophilic carbon and a bad leaving group

(d) they have a nucleophilic carbon and a good leaving group

(vi) Which one of the following is not a nucleophile:

(a) H_2O (b) H_2S (c) BF_3 (d) NH_3

(vii) Double bond is formed as a result of:

(a) Substitution reactions (b) Elimination reactions

(c) Addition reactions (d) Rearrangement reactions

(viii) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen

(a) RBr (b) RCl (c) RF (d) RI

(ix) CH_3CH_2Br on treatment with alc. KOH gives:

(a) Propanal (b) Propene (c) Propane (d) None

(x) Grignard's reagent gives alkane with,

(a) Water (b) Ethylamine (c) Ethanol (d) All of these

(xi) Action of alkyl halides with Na metal yield,

(a) Alkanes (b) Alcohols (c) Alkenes (d) Phenols

(xii) Alkyl halides react with excess of ammonia to give;

(a) 1° amine (b) 2° amine (c) 3° amine (d) [illegible]

(xiii) Among the alkyl halides the primary alkyl halides always follow the mechanism.

(a) SN_1 (b) SN_2 (c) SN (d) SN

(xiv) Grignard's regent on treatment with chloramines gives:

(a) Acetamide (b) Primary amine (c) Secondary amine (d) [illegible]

(xv) Nucleophilic addition of a primary amine giving;

(a) Imine (b) urea (c) ammonia (d) Nitrobenzene

ANSWERS TO MULTPLE CHOICE QUESTIONS

(i) Ans: (c) One

By definition the primary carbon atom is directly attached to one carbon atom. e.g. in CH_3-CH_2-Br the carbon atom attached to Br is the primary carbon atom

(ii) Ans: (a) Primary alkyl halides

Since primary alkyl halides have [illegible] the nucleophile can easily attack [illegible] leaves in one step. Such type [illegible]

(iii) Ans: (d) E1 and S_N2

(iv) Ans: (a) the concentration of substrate

(v) Ans: (b) they have an electrophilic carbon and a good leaving group

(vi) Ans: (c) BF_3

(vii) Ans: (b) Elimination reactions

(viii) Ans: (d) HI

(ix) Ans: (b) Propene

(x) Ans: (d) All of these

(xi) Ans: (a) Alkenes

(xii) Ans: (d) all

(xiii) Ans: (b) S_N2

(xiv) Ans: (a) 1°-amine

(xv) Ans: (a) Imine

Q2: Give brief answers for the following questions.

(i) What are primary, secondary and tertiary alkyl halides?

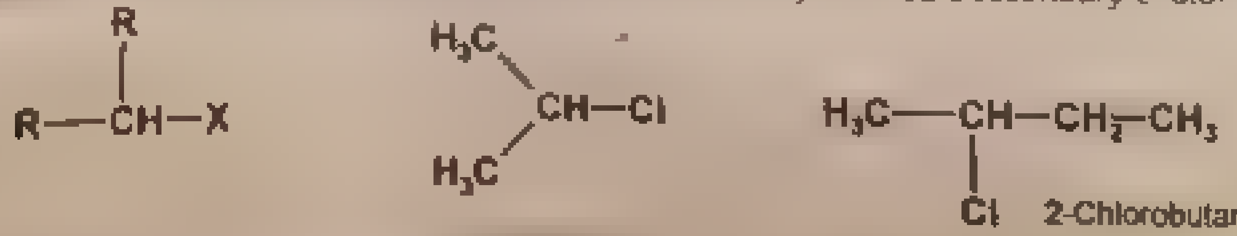
(i) Primary Alkyl Halides

Alkyl halide in which halogen atom is attached with primary carbon are called primary halides. A primary C-atom is attached to one or no carbon atom is called a primary C-atom.

$R-CH_2-X$ $\quad$ CH_3-Cl (Methyl chloride) $\quad$ CH_3-CH_2-Cl (Ethyl chloride) $\quad$ $CH_3-CH_2-CH_2-Cl$ (n-Propyl chloride)

(ii) Secondary Alkyl Halides

Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide. A Secondary C-atom is attached to two C-atoms simultaneously is called a secondary C-atom.



2-Chloropropane $\quad$ 2-Chlorobutane

(iii) Tertiary Alkyl Halides:

Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halides.
A tertiary C-atom is attached to three C-atoms simultaneously, is called tertiary carbon.

2-Chloro-2-methylpropane

(i) Why alkyl iodides cannot be prepared by directly heating iodine with alkane?

The alkyl iodides cannot be obtained directly by heating alkanes with iodine.

It is because when an alkane reacts with iodine, alkyl iodide and HI are produced. The HI is a strong reducing agent. So it reduces the product alkyl iodide back to the original alkane.

$$CH_4 + I_2 \xrightarrow[\text{UV light}]{h\nu} CH_3{-}I + HI$$

$$CH_3{-}I + HI \longrightarrow CH_4 + I_2$$

(iii) What are Nucleophilic substation reactions or SN reaction?

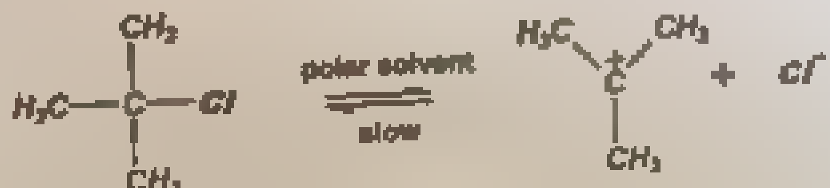
The reaction in which a nucleophile replaces another atom or a group of atom already present in a molecule are called nucleophilic substitution reactions.

General process of S_N reactions is

(iv) Tertiary alkyl halides show S_N1 reactions mostly, why?

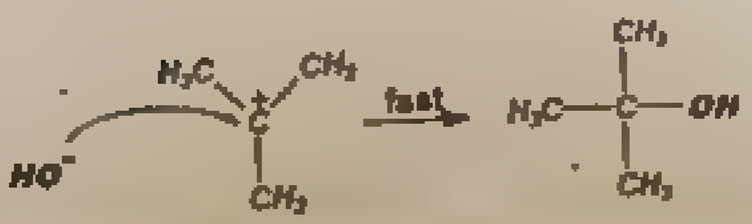
- In tertiary alkyl halides, the tertiary carbon atom is surrounded by bulky alkyl groups. Therefore, [illegible] for a nucleophile to reach this carbon. Hence, S_N2 reaction cannot occur with tertiary alkyl halides.
- The tertiary alkyl halides first undergo ionization. During this process leaving group leaves and the tertiary carbon becomes sp^2 hybridized with angle 120°. Thus, nucleophile easily attacks the tertiary carbon [illegible]. Therefore, S_N1 reaction occurs with tertiary alkyl halides. The reaction complete in two steps.

Step - 1



Carbocation

Step - 2



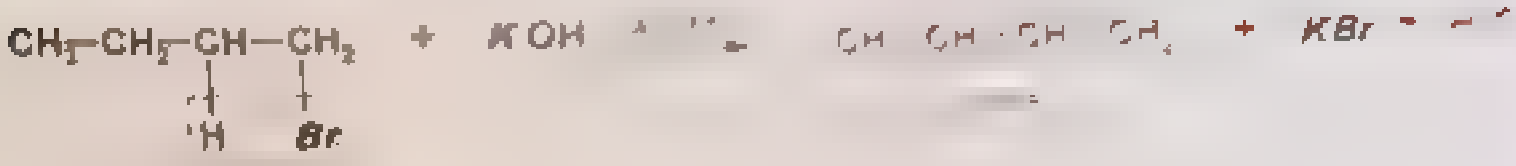
(v) **What are elimination reactions**

The chemical reaction in which two groups are ... elimination reaction

When β hydrogen is eliminated ...

Examples.

Alkyl halides on heating with a ...



1 Bromobutane

(vi) Which factor decides the reactivity of alkyl halides?

There are two main factors whi...

(i) Bond Polarity

The molecule of alkyl halide is polarized due ... Hence carbon acquires partial ... nucleophilic in character which can be replaced by another nucleophile

(ii) Bond Energy

Experiments have shown that the bond energy of C-X bond is the ... alkyl halides, and not the polarity of the molecule

A study of bond energies of C-X bond shows that C-F bond is the stronge...

So the overall order of reactivity ...

R-iodide > R-bromide > R-chloride > R-fluoride

(vii) What are the diazonium salt?

When amines react with nitrous acid diazonium compounds ...

$$R-NH_2 + HNO_2 \longrightarrow R-\overset{+}{N}\equiv N + HO^- + H_2O$$

Diazonium ion

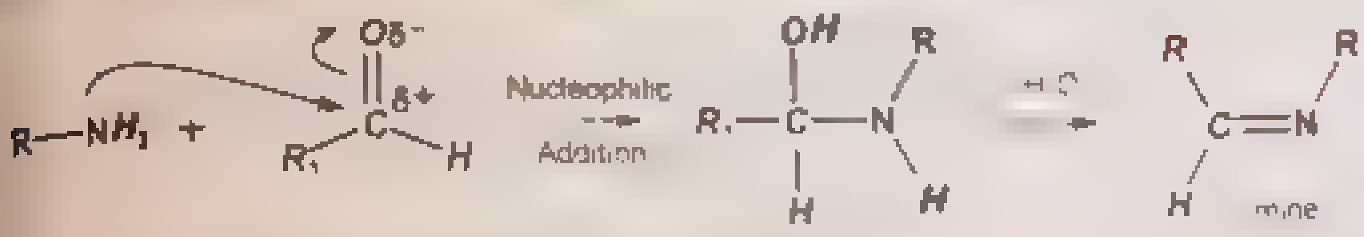
The diazonium group, group is ustable In the case of the ethyl ...

$$CH_3-CH_2-\overset{+}{N}\equiv N \longrightarrow N_2 + [CH_3-\overset{+}{C}H_2] \xrightarrow{H_2O} CH_3-CH_2-OH + H^+$$

$$\longrightarrow CH_2=CH_2$$

When the group is attached to a benzene ring, the ion is stabilized to some extent by the ... the ring The benzenediazonium ion is therefore much more stable than aliphatic However ... readily above 10°C.

(viii) How can nucleophilic addition of a primary amine giving an imine?

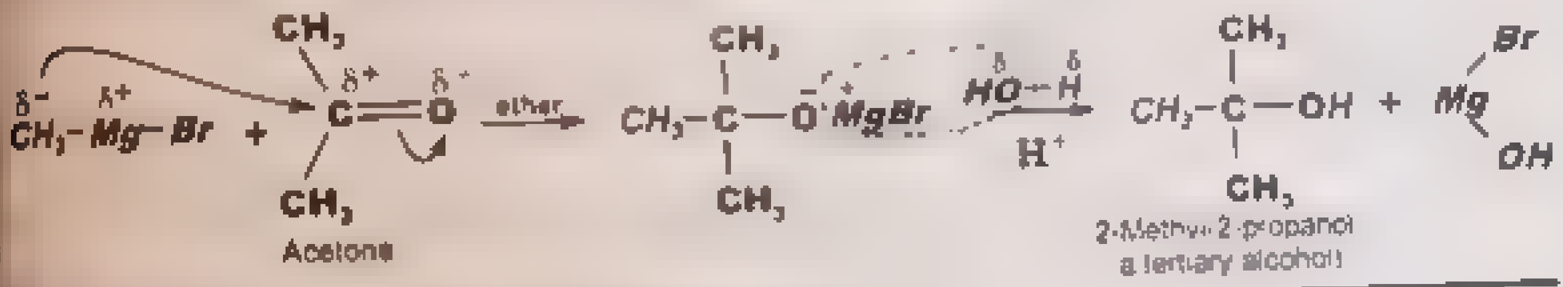


(ix) Amines are more basic than analogous alcohols why?

Amines may act as bases towards acids [illegible] It is because they have single electron pair on nitrogen atom which is [illegible] alcohols. There are two lone pairs of electrons on oxygen atom. These [illegible] with each other during donation. Hence, neither of these two is [illegible] bases than amines.

(x) How tertiary alcohols are obtained from R Mg-X?

Tertiary alcohols are obtained by the reaction of R-Mg-X [illegible] e.g.



Q3: Give detailed answers for the following questions.

(i) Discuss the reactivity of alkyl halides

Page 226

(ii) Give three methods for the preparation of alkyl halides

Page 226

(iii) Explain in detail S_N1 and S_N2 reactions with mechanism

Page 231

(iv) What are β-elimination reactions? Explain them with detail

Page 234

(v) How will you convert ethyl chloride to the

(a) Ethyl cyanide

$$CH_3-CH_2-Cl + KCN \longrightarrow CH_3-CH_2-CN + KCl$$

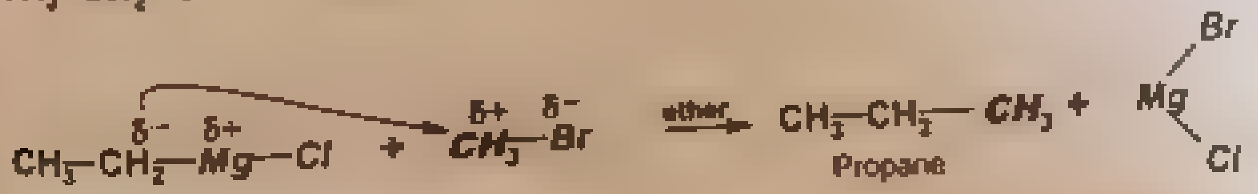
Ethyl cyanide

(b) Ethanol

$$CH_3-CH_2-Cl + KOH \xrightarrow{\text{aqueous}} CH_3-CH_2-OH + KCl$$

(c) Propane

$$CH_3-CH_2-Cl + Mg \xrightarrow{\text{ether}} CH_3-CH_2-Mg-Cl$$



(d) n Butane

$$CH_3-CH_2-Cl + 2\,Na + Cl-CH_2-CH_3 \xrightarrow{ether} CH_3-CH_2-CH_2-CH_3 + 2\,NaCl$$

(d) Tetraethyl lead

$$\underset{\text{Ethyl chloride}}{4\,C_2H_5Cl} + Na_4Pb \longrightarrow \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + 4\,NaCl$$

(vi) Discuss the preparation and reactivity of Grignard's reagent

Page 240

(vii) What are the amines? Give its nomenclature

Page 244

(viii) What are the main features which increase the basicity of amine?

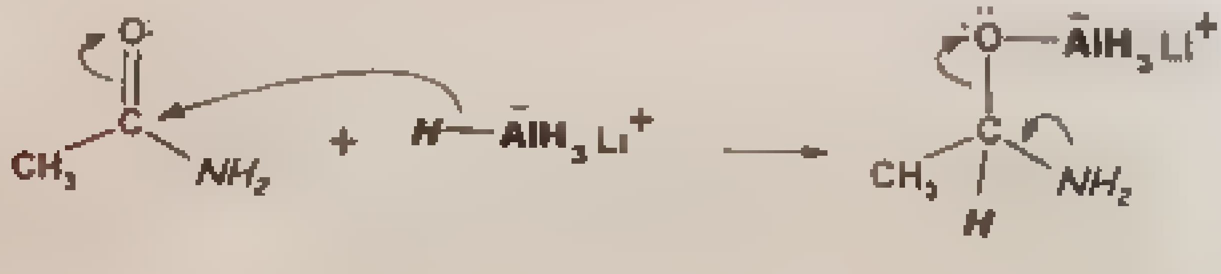
Page 250

(ix) Amides are reduced by $LiAlH_4$. Give mechanism.

Reaction.

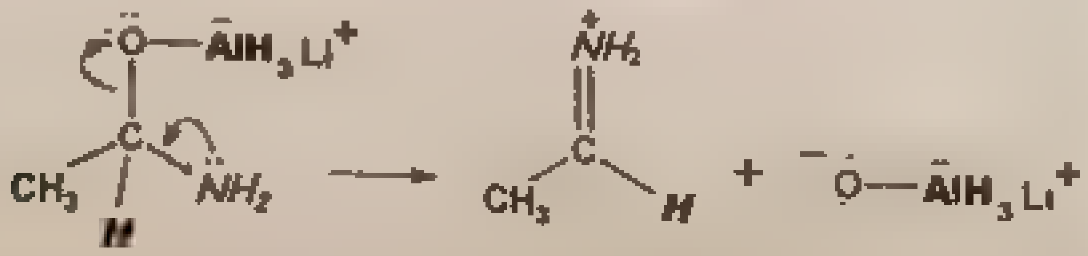
Mechanism

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl gr the amide
- The electrons from the C=O move to the electronegative O creating an intermediate metal alk complex



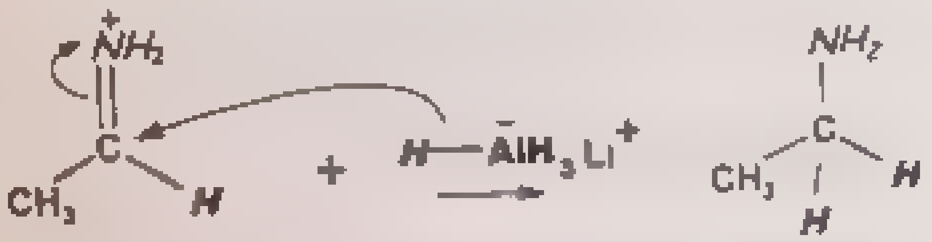
Step 2:

- The tetrahedral intermediate collapses and displaces the O as part of a metal alkoxide leaving group
- This produces a highly reactive iminium ion an intermediate



Step 3:

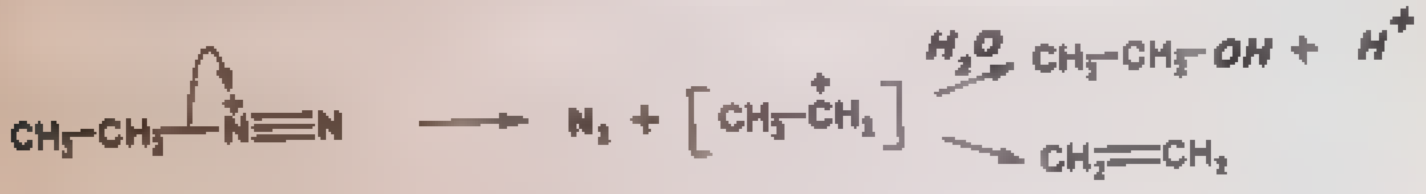
- The nucleophilic H from the hydride reagent adds to the electrophilic C in the iminium system.
- The π-electrons from the C=N move to the cationic N to neutralize the charge. Thus amine is produced.



(x) What are the diazonium salts? How they can be prepared? Give their reactions?

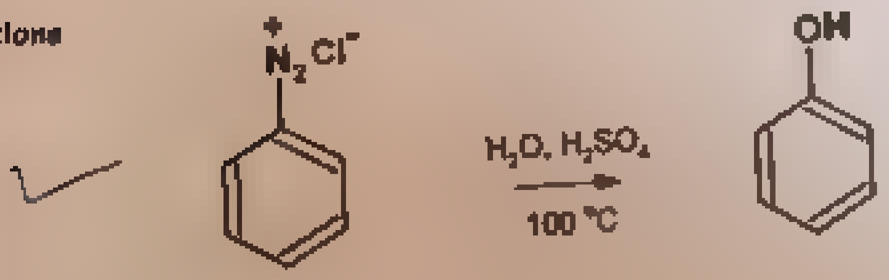
When amines react with nitrous acid, diazonium compounds are formed.

The diazonium group group is rather unstable. In the case of the ethyl diazonium ion, it decomposes at once.



When the group is attached to a benzene ring, the ion is stabilized to some extent by the delocalized electron of the ring. The benzenediazonium ion is therefore much more stable than aliphatic. However, it also decomposes readily above 10°C.

Reactions



TEST YOUR SKILLS

[illegible]

Time 20 Minutes Marks 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Q1 Circle the correct option i.e. A B C D Each part carries one mark

i) [illegible]
A Electrophilic **B Nucleophilic** [illegible]

ii) In $CH_3COCH_3 + CH_3MgI$ ⟶ Intermediate + H_2O ⟶
This X [illegible]
A CH_3OH B C_2H_5OH C CH_3CN **D Tertiary butyl alcohol**

iii) Which reagent [illegible]
A HF [illegible] **B NaCl** [illegible]

iv) Treatment of [illegible]
A Triethyl amine B [illegible] C [illegible] **D Tetraethyl ammonium chloride**

v) Alkyl fluorides are less reactive [illegible]
A. high bond energy B [illegible] C [illegible] D [illegible]

vi) For the reaction [illegible]
The order of reactivity [illegible]
A HBr > HI > HF **B. HI > HBr > HCl** C [illegible] D [illegible] > HBr > HI

vii) When alkyl magnesium [illegible]
A 2 butanol **B 1-butanol** C [illegible] D [illegible]

viii) Grignard reagent [illegible]
A Organo [illegible] **B. Organo-magnesium compounds**
C Organo-zinc compounds D [illegible]

ix) Which one of the following is an [illegible]
A NH_3 B. H_2O C Cl_2 **D. BF_3**

x) What is shape of carbocation?
A Linear B. Planar Square **C planar** D Tetrahedral

xi) Double bond is formed as result of [illegible]
A Substitution reaction B **B. Elimination reactions**
C Addition reactions D [illegible]

xii) The common name of 2-methyl-2 chloropropane [illegible]
A Isobutyl chloride B sec-butyl chloride **C. ter-butyl chloride** D n-butyl chloride

xiii) E2 reaction obeys
A First order kinetics **B Second order kinetics** C Third order kinetics D Zero order kinetics

xiv) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen
A RBr B RCl C RF **D. RI**

xv) CH_3CH_2Br on treatment with alc KOH gives
A Propanal B Propene C Propene **D. None**

xvi) Grignard's reagent gives alkane with
A Water B Ethylamine C Ethanol **D. all of these**

xvii) Action of alkyl halides with Na metal yield
A. Alkanes B Alcohols C Alkenes D Phenols

SUBJECTIVE

Time: 2:35 Hours

Total Marks Section B and C 68

Section – B (Marks 42) (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines

i) Alkyl halides are considered amongst the most reactive class of organic compounds Consider the equation

$$(CH_3)_3Cl \xrightarrow[\text{Polar solvent}]{\text{Base}} (CH_3)_3OH$$

a Suggest the name and mechanism involved for the above conversion 01
b What will happen to the configuration of alkyl halide during the process? 01
c Write rate equation for this reaction. 01

ii) a How does nature of alkyl group change when alkyl halide is converted into Grignard's reagent 01
b Why is the dry ether necessary for the preparation of Grignard's reagent? 01
c How does the primary alcohol produce when ethylene oxide reacts with Grignard's reagent 01

iii) How is Grignard Reagent used for the preparation of alkanes? Give any three examples with reaction

(iv) a. Write two methods for the preparation of alk...
b. What are primary secondary and tertiary ...

(v) a. Why alkyl iodides cannot be prepared ...
b. Thionyl chloride $SOCl_2$ is the best reagent ...

(vi) a. How alkyl iodides are prepared
b. Which factor decides the reactivity of alkyl halides
c. Define an electrophile and a nucleophile

(vii) a. Explain the given order of reactivity 03

R-I > R-Br > R-Cl > R-F

(viii) a. What products are formed when the following compounds are treated with Eth...

A. HCHO B. $(CH_3)_2CO$

b. Why Grignard's reagent is highly reactive

(ix) a. What are Nucleophilic substitution reactions or S_N reactions
b. Why primary alkyl halides always follow S_N2 mechanism? 01
c. Tertiary alkyl halides show S_N1 reactions mostly. Why? 01

(x) a. S_N2 reactions shows 2^{nd} order kinetics, why
b. Why the configuration of the product is inverted during S_N2 ...
c. Why there is 50% inversion and 50% retention in the prod...

(xi) a. Write down the t-butyl bromide with KOH in aqueous medium
b. What are β-Elimination reactions? 01

(xii) a. What is Wurtz synthesis?
b. Why all reagents must be dry during the preparation of Grignard's reagent?

(xiii) a. Draw all the possible isomers of $C_5H_{11}Cl$ and classify them as primary, secondary and tertiary 03

(xiv) a. How carboxylic acids are obtained from Grignard's reagent?
b. How tertiary alcohols are obtained from R-Mg-X?
c. How tetraethyl lead is obtained from alkyl halides? 1

(xv) a. What is a carbocation? Write two methods for its generation? 02
b. How alkyl halides can be prepared from alkenes?

(xvi) a. Write mechanism of E2 reaction. 01
b. Give two methods to produce primary alcohols from Grignard's reagent 02

(xvii) a. Differentiate between E1 and E2 reaction 2
b. How may Grignard's reagent may be prepared in laboratory?

(xviii) a. Iodide ion is both a good leaving group and a good nucleophile. Explain why? 02
b. How may PCl_5 be used for the preparation of alkyl halides? 01

(xix) a. How alkyl halides can be reduced to alkanes? 01
b. How alkenes may be converted into alkyl halides? 01
c. What is the effect of nature of alkyl group on the preparation of Grignard's reagent? 01

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

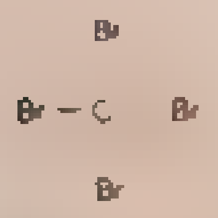
Q 5 a. Discuss the reactivity of alkyl halides 04
b. Discuss classification of alkyl halides 03
c. Chloroethene can be obtained from Ethene in the laboratory by the following route

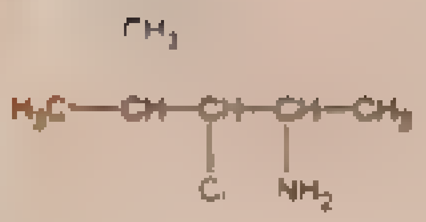
$CH_2 = CH_2 \xrightarrow{(I)} Cl\text{-}CH_2 - CH_2\text{-}Cl \xrightarrow{(II)} CH_2 = CH - Cl$

(i) Describe the conditions necessary for each of the reactions I and II 02
(ii) Describe the steps in the mechanism of reaction I. 03

Q. 4 [illegible]

Q. 5 [illegible]



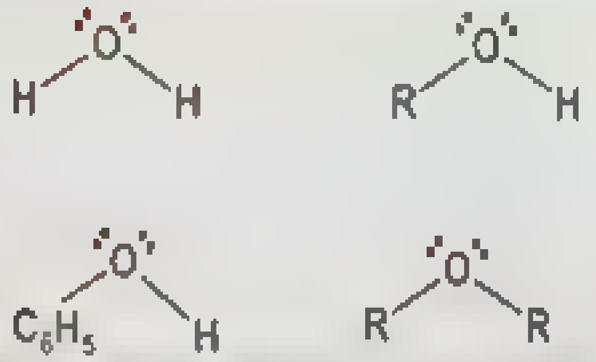


iv

c. How ethyl magnesium bromide reacts with 05
(i) NH_3 (ii) Alcohols (iii) CO_2 (iv) Aldehydes (v) Acetone

CHAPTER # 18

ALCOHOLS, PHENOLS AND ETHERS



INTRODUCTION

The structure of alcohols, phenols and ethers are [illegible]

Alcohols and phenols both contain hydroxyl –OH group attached to alkyl and phenyl groups respectively. In ether both hydrogen atoms of water are replaced by alkyl or phenyl groups.

ALCOHOLS

The aliphatic organic compounds containing hydroxyl group –OH, as functional group are called alcohols.

Monohydric alcohols: Alcohols containing one –OH group are called monohydric alcohols.

Polyhydric alcohols: The alcohols containing two or more hydroxyl groups are known as polyhydric alcohol.

Classification of Monohydric Alcohols.

Monohydric alcohols are classified into the following three families.

(i) Primary alcohols:

In these, carbon atom attached to OH group, is directly attached to one or no carbon atom.

CH_3-OH Methanol

CH_3-CH_2-OH Ethanol

$CH_3-CH_2-CH_2-OH$ 1-Propanol (n-propyl alcohol)

(ii) Secondary alcohols:

In these, carbon atom attached to OH group, is directly attached to two carbon atoms.

$$\begin{array}{l} CH_3-CH-OH \\ \quad\quad\;\; | \\ \quad\quad CH_3 \end{array}$$

2-Propanol (sec-Propyl alcohol)

$$\begin{array}{l} CH_3-CH_2-CH-OH \\ \quad\quad\quad\quad\quad\; | \\ \quad\quad\quad\quad\;\; CH_3 \end{array}$$

2-Butanol (sec-Butyl alcohol)

(iii) Tertiary alcohols:

In these, carbon atom attached to OH group, is directly attached to three carbon atoms.

$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ CH_3 \end{array}$$

2-Methyl-2-propanol (ter-Butyl alcohol)

NOMENCLATURE OF ALCOHOLS:

1. Common System of Naming

Examples

CH_3OH Methyl alcohol — $C_6H_5CH_2OH$ Benzyl alcohol

2. IUPAC System

i. ... group is selected as the parent hydrocarbon

ii. ... replaced by ol

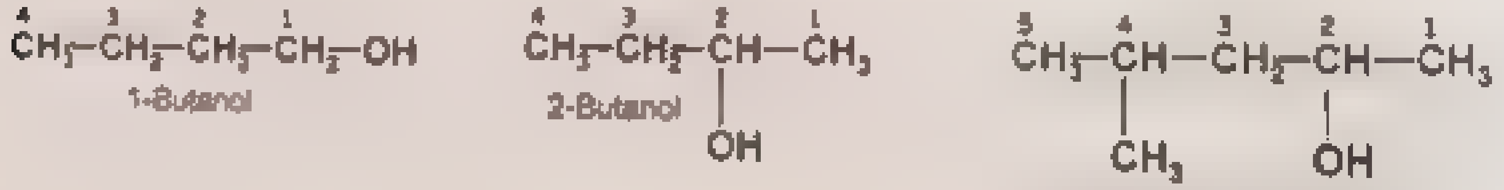
iii. ... placing the number of carbon to which –OH is attached ...

iv. ... –OH group is numbered beginning from that end which would assign ... lowest possible number to carbon atom linked to the –OH group

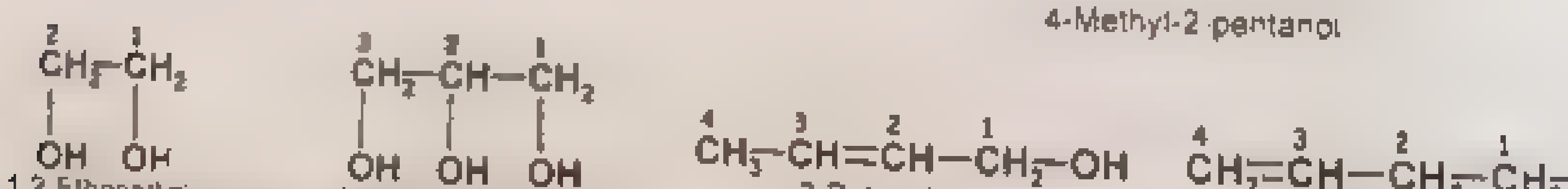
v. The presence of more than one –OH groups is indicated by suffixes –diol, –triol etc. and repeat ... number of carbon atoms to which –OH groups are attached

vi. In unsaturated alcohols the hydroxy group gets the lower number rather than unsaturation e.g.

Examples



1-Butanol — 2-Butanol — 4-Methyl-2-pentanol

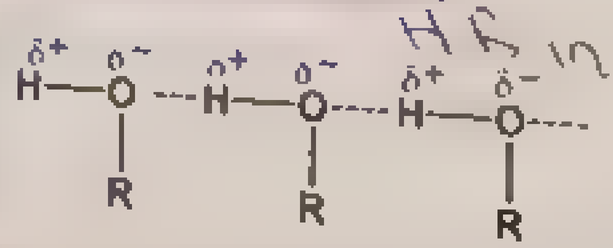


1,2-Ethanediol — 1,2,3-Propanetriol — 2-Buten-1-ol — 3-Buten-1-ol

PHYSICAL PROPERTIES:

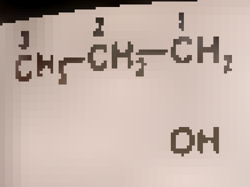
- Alcohol upto butanols are generally colorless liquids. These have characteristic sweet smell and ... taste. They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but decreases in higher alcohol

H.B in alcohol

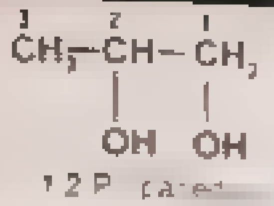


- Melting and boiling points of alcohols are higher than corresponding alkanes. It is due to hydrogen bonding which is present in alcohols but absent in alkanes

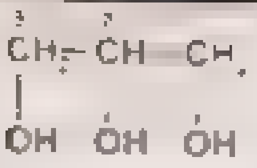
MORE PRACTICE

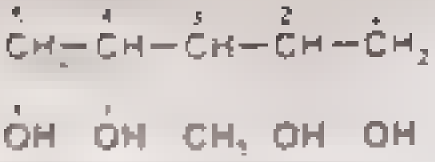


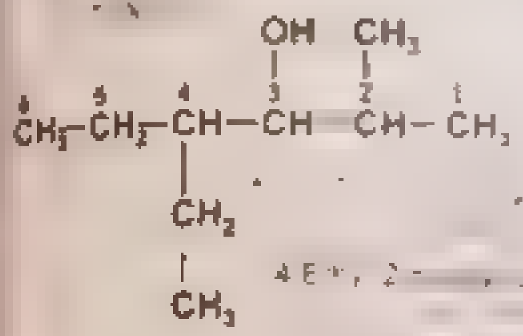
1-Propanol

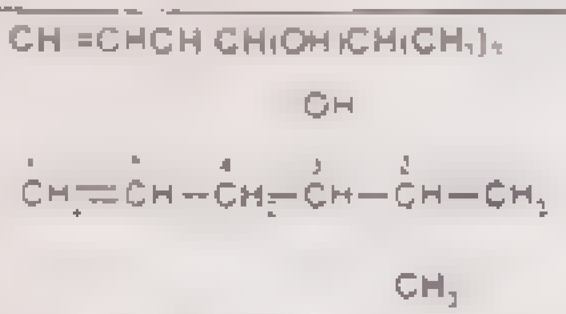


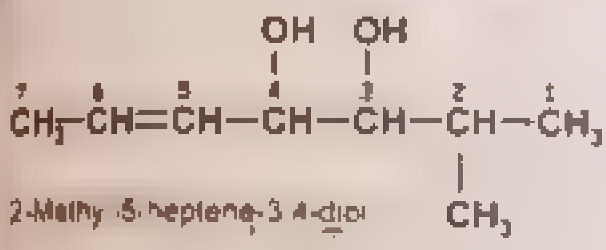
1,2-Propanediol



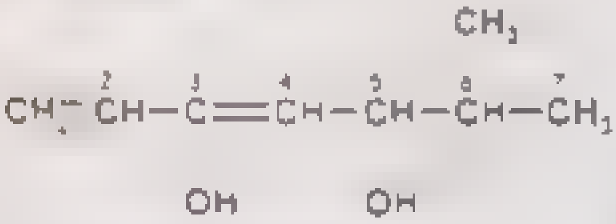


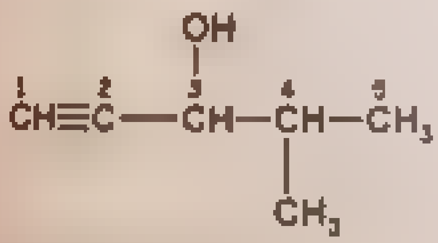




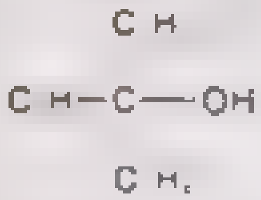


2-Methyl-5-heptene-3,4-diol



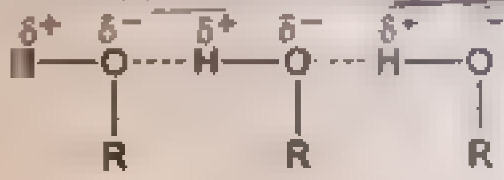


4-Methyl-1-pentyn-3-ol



STRUCTURE

- The alcohol functional group consists of an O atom bonded ...
- Both the C O and the O-H bonds are polar due to the ...



ACIDITY

- Due to the electronegativity of the O atoms, alcohols are s...
- The anion derived by the deprotonation of an alcohol is the **alkoxide ion**, RO
- Alkoxides are important bases in organic chemistry
- Alcohols react with Na (or K) like water to give the alkoxide

$$2\,ROH + 2\,Na \longrightarrow 2\,NaOR + H_2$$

Sodium alkoxide

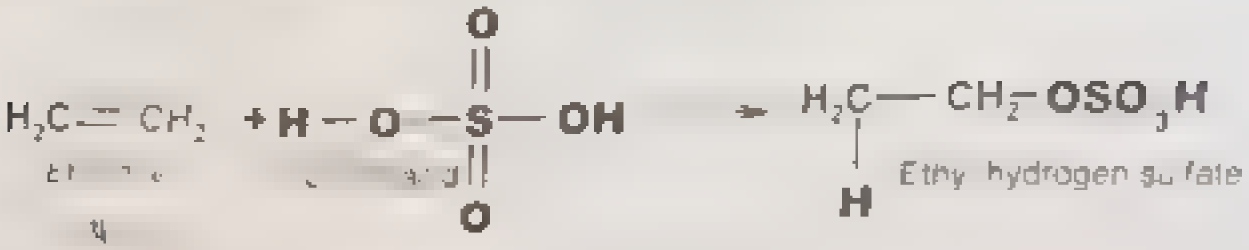
2 R — O — H + Na

$$2\,HOH + 2\,Na \longrightarrow 2\,NaOH + H_2$$

2 H — O — H

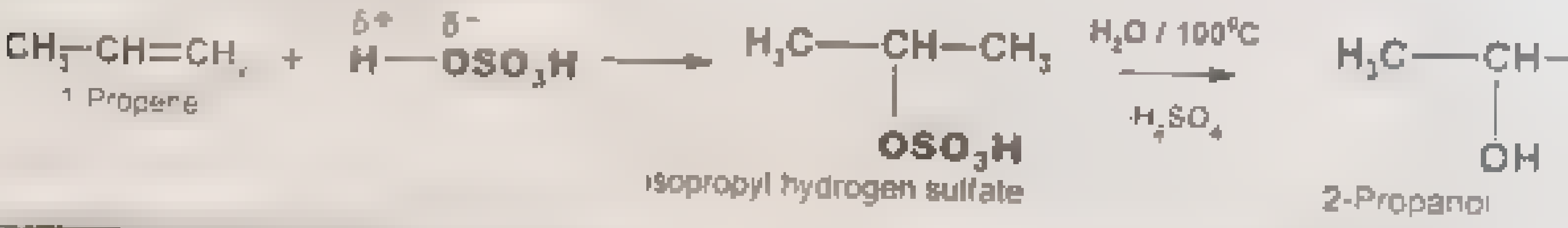
PREPARATIONS OF ALCOHOLS

(1) HYDRATION OF ALKENES



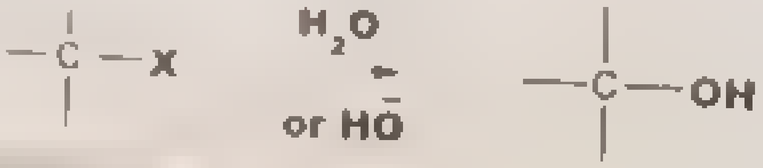
On ... by heating alkyl hydrogen sulphates are hydrolyzed to alcohols

The reaction follows Markownikoff ...



(2) HYDROLYSIS OF ALKYL HALIDES

- Alkyl halides can be converted to alc... water or hydroxide as the nucleophile



- ... substitution

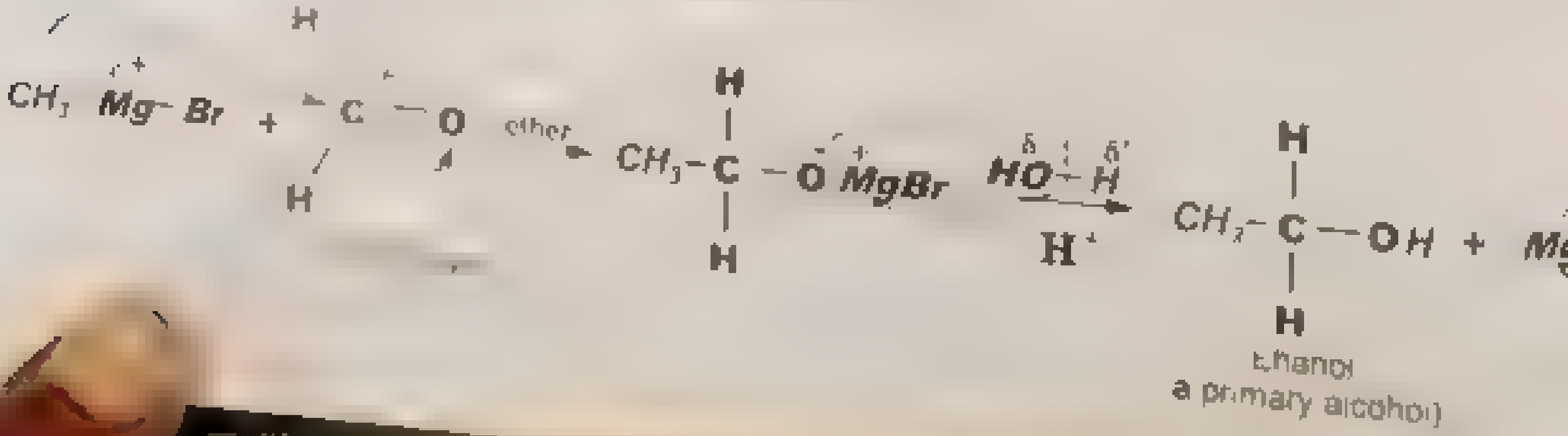
Quick Quiz ... Grignard's reagent is used for the preparation of alcohols

REACTIONS OF R-MgX OR RMgX WITH ALDEHYDES AND KETONES

- ...
- ... can be prepared by the ... of Grignard reagent ... and the resulting compound ...

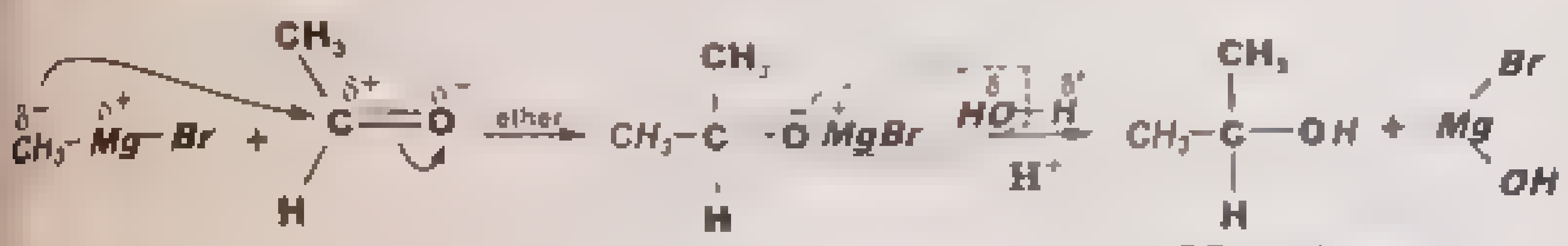
(a) Primary alcohol

Formaldehyde ...



(b) Secondary Alcohols

All aldehydes except formaldehyde give secondary alcohols with Grignard's reagent.

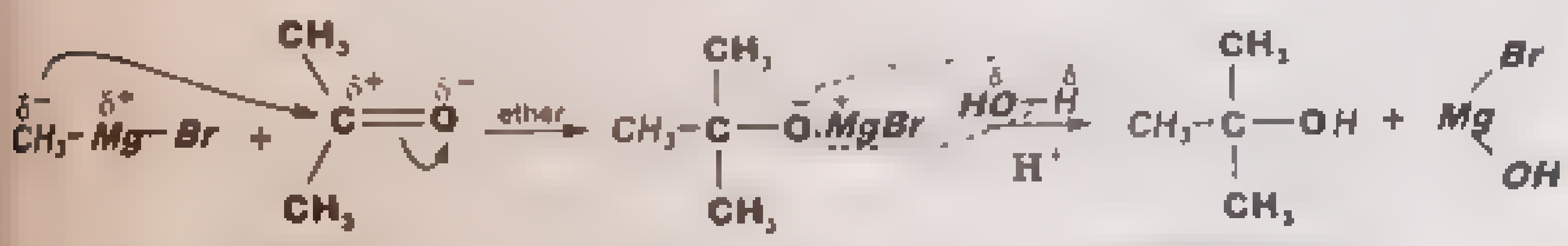


Acetaldehyde

2-Propanol (a secondary alcohol)

(c) Tertiary Alcohols

Ketones give tertiary alcohols with Grignard's reagent.



Acetone

2-Methyl-2-propanol a tertiary alcohol

(4) REDUCTION OF ALDEHYDES AND KETONES

Reduction of aldehydes, ketones and carboxylic acid esters in the presence of Ni, Pd or Pt gives alcohols

Acetaldehyde

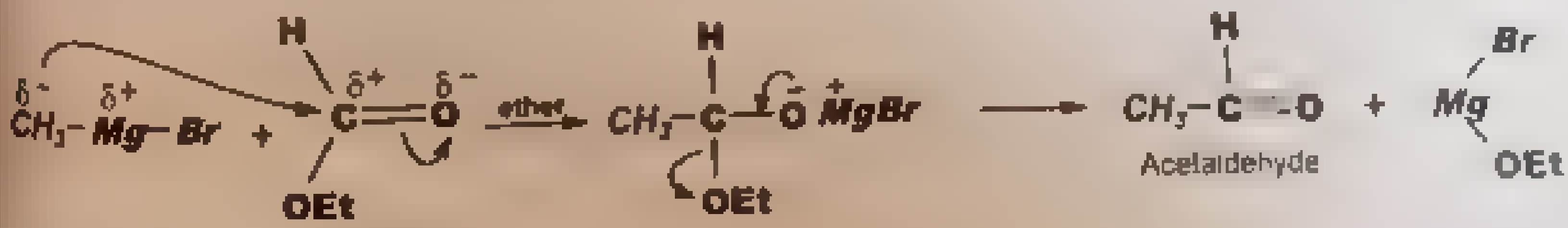
Ethanol

$LiAlH_4$ can also reduce carboxylic acids as well as aldehydes, ketones and ester

$$RCOOH + LiAlH_4 \rightarrow RCH_2OH$$

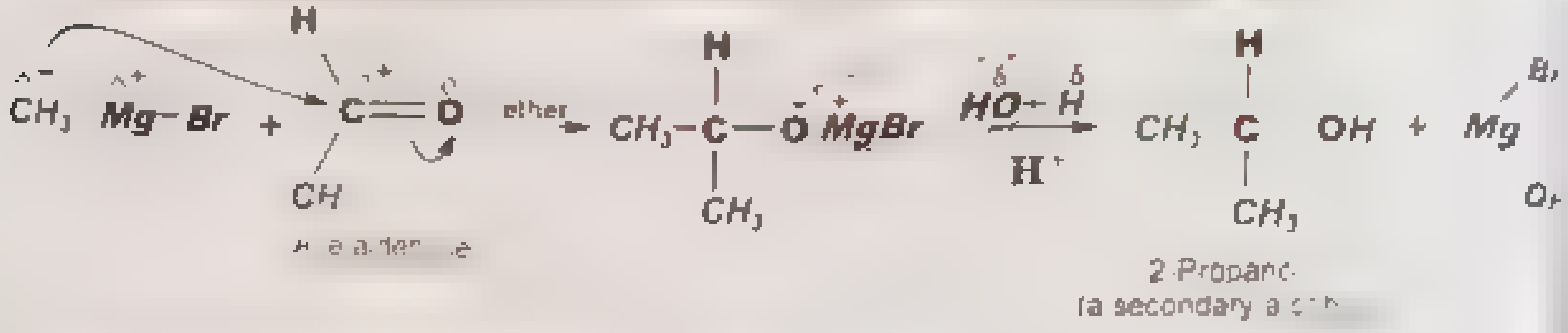
(5) REACTION OF RLi OR RMgX WITH ESTERS

Esters react with Grignard reagents to form alcohols.

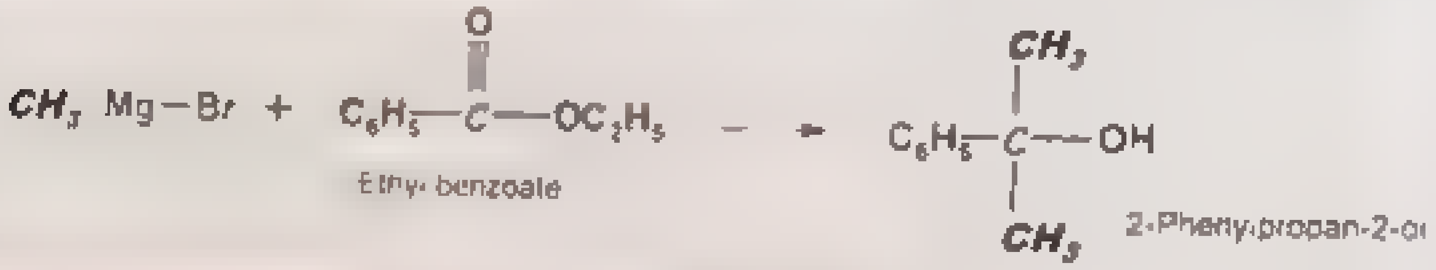


Ethyl formate

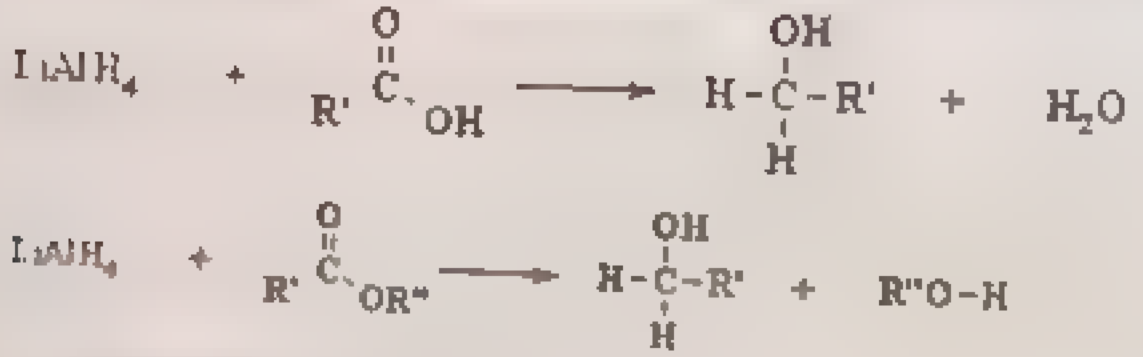
Acetaldehyde



Similarly, other ... tertiary alcohols with Grignard's Reagents.



(6) REDUCTION OF CARBOXYLIC ACIDS AND ESTERS



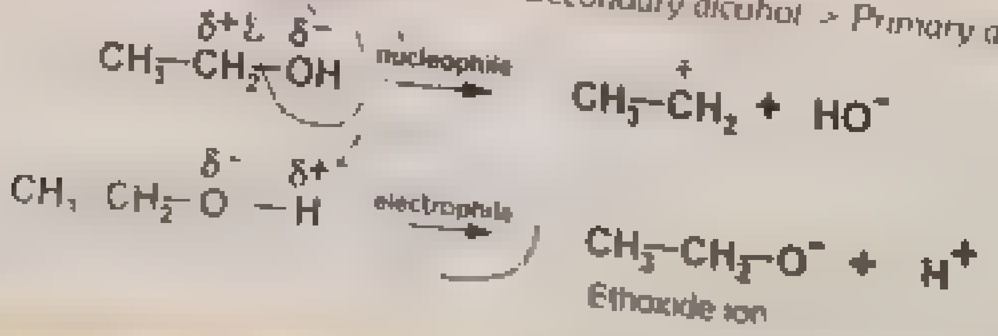
- Carboxylic acids ... esters are less reactive to **Nucleophiles** than aldehydes or ketones. So, they can only be reduced by $LiAlH_4$ and **NOT** by the less reactive $NaBH_4$
- Each reaction requires that 2 hydrides be added to the carbonyl of acids or esters

REACTIVITY:

- Alcohol reacts with other reagents due to the breaking of C-O and O-H bonds
- Breaking of bonds depends upon the nature of the attacking reagent
- If a nucleophile attacks, the C-O bond breaks
- The order of reactivity of alcohols with respect to cleavage of C-O bond is

  Tertiary alcohol > Secondary alcohol > Primary alcohol
- If an electrophile attacks the O-H bond breaks
- The order of reactivity of alcohol with respect to O-H bonds cleavage

  CH_3OH > Tertiary alcohol > Secondary alcohol > Primary alcohol



REACTIONS OF ALCOHOLS

(1) REACTION WITH HX

- Due to the presence of unshared electron pairs on the oxygen [illegible] bases [illegible] react with halogen acids to form their respective alkyl halides

$$R-OH + H-Br \longrightarrow R-Br + H_2O$$

- The C-O bond in an alcohol is very slightly polarized. Therefore the [illegible] mechanism is not possible

$$\overset{\delta+}{R}-\overset{\delta-}{OH} + \overset{\delta+}{H}-\overset{\delta-}{Br} \not\longrightarrow R-Br + H_2O$$

- In fact, the alcohol first acts as a base, it accepts proton from HX to [illegible] ion. Now the C-O bond becomes highly polarized. Thus, the electrophilic carbon [illegible] easily attacked by a nucleophile to break C-O bond

$$R-\ddot{O}(H): + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow R-\overset{+}{O}(H)-H + Br^-$$

Alkyloxonium ion

$$Br^- + R-\overset{+}{O}(H)-H \longrightarrow R-Br + H_2O$$

- The orders of reactivity of halogen acids HI > HBr > HCl
- The orders of reactivity of alcohols is ter-alcohol > sec-alcohol > prim-alcohol
- HCl and prim-alcohol are the least reactive amongst halogen acids and alcohols respectively. Therefore they react only in the presence of a catalyst. A solution of $ZnCl_2$ in concentrated [illegible] used as a catalyst

$$\underset{\text{Primary alcohol}}{R-CH_2-OH} + H-Cl \xrightarrow[\text{heat}]{ZnCl_2} R-CH_2-Cl + H_2O$$

Mechanism

attach

$$R-\ddot{O}(H): + ZnCl_2 \longrightarrow R-\overset{+}{O}(H)-\overset{-}{Zn}Cl_2$$

separation

$$R-\overset{+}{O}(H)-\overset{-}{Zn}Cl_2 \longrightarrow R^+ + H-O-\overset{-}{Zn}Cl_2$$

attach

$$H-\ddot{O}-\overset{-}{Zn}Cl_2 + H-Cl \longrightarrow H_2O + ZnCl_2 + Cl^-$$

separation

$$R^+ + Cl^- \longrightarrow R-Cl$$

attach

Exercise Q3 How will you distinguish between ... reactions

LUCAS TEST

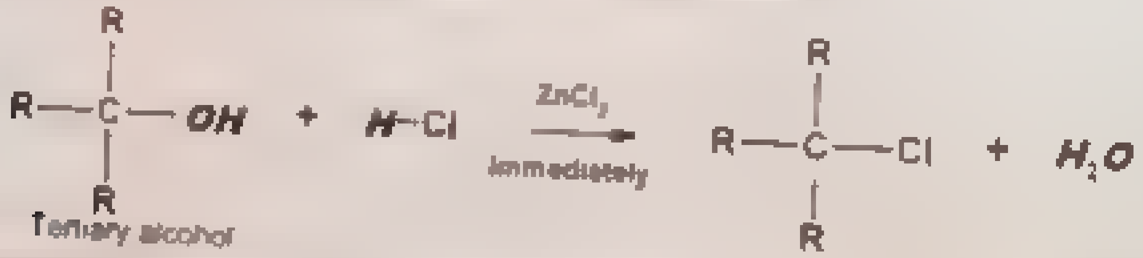
- ...
- ...

(i) ...

$$R-CH_2-OH + H-Cl \xrightarrow{ZnCl_2} R-CH_2-Cl + H_2O$$

(ii) Secondary alcohol for...

(iii) Primary alcohol forms an insoluble pr...



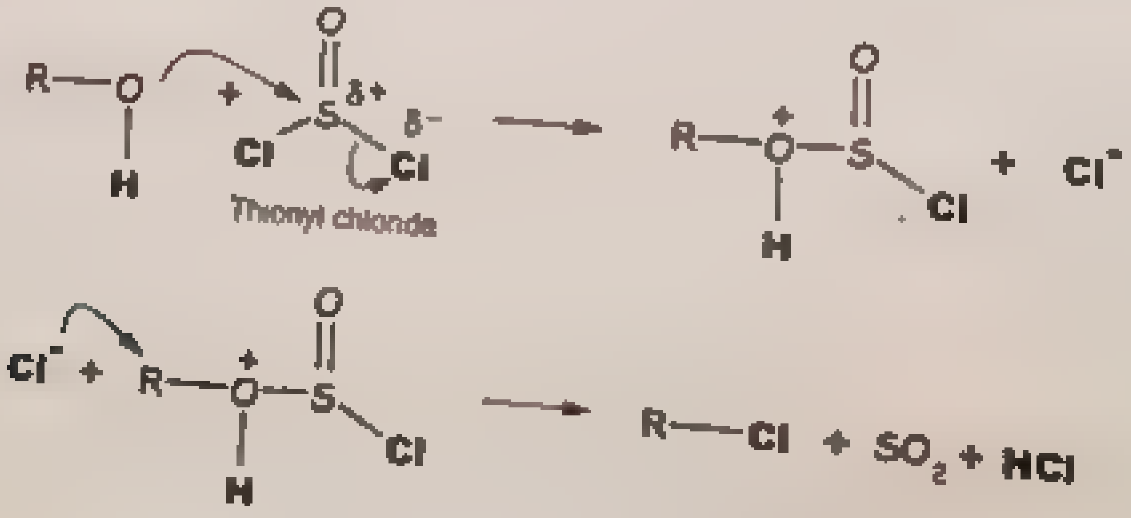
(2) REACTION WITH $SOCl_2$, PX

(i) Thionylchloride ($SOCl_2$)

Alcohols react with thionylchloride to give alkyl chlorides

$$R-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{pyridine}} R-Cl + SO_2 + HCl$$

Mechanism



(ii) Phosphorus Tribromide and Triiodide (PBr_3 and PI_3)

Alkyl bromides and iodides are [illegible]

$$3R-OH + PI_3 \longrightarrow 3R-I + H_3PO_3$$

$$3R-OH + PBr_3 \longrightarrow 3R-Br + H_3PO_3$$

3) ACID CATALYZED DEHYDRATION

Ethers are produced via acid-catalyzed deh[illegible]

$$2\ -\overset{|}{\underset{|}{C}}-OH \xrightarrow[\text{heat}]{H^+} -\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{C}}- \quad H_2O$$

- Reagents are typically H_2SO_4 and heat
- The method is limited to **symmetrical** ethers of **primary** [illegible]
- The method is not suitable for unsymmetrical ethers

MECHANISM

Step 1.

The lone pairs on the oxygen make it a Lewis [illegible] acid base reaction. The alcohol oxygen is protonated to make a better leaving group [illegible] fast and reversible

$$CH_3-CH_2-\ddot{O}H \overset{H^+}{\rightleftharpoons} CH_3-CH_2-\overset{+}{O}(H)-H$$

Step 2.

The O of the second alcohol molecule functions as the nucl[illegible] group (H_2O) by breaking the C-O bond. This forms an ox[illegible]

$$CH_3-CH_2-\ddot{O}H + CH_3-CH_2-\overset{+}{O}(H)-H \longrightarrow CH_3-CH_2-\overset{+}{O}(H)-CH_2-CH_3 + H_2O$$

Step 3.

This is another acid – base reaction. The proton is removed by a [illegible] molecule removes the proton. The alcohol ROH can also do this. Thus [illegible]

$$CH_3-CH_2-\overset{+}{O}(H)-CH_2-CH_3 + H_2O \rightleftharpoons CH_3-CH_2-O-CH_2-CH_3 + H_3\overset{+}{O}$$

4) PREPARATION OF ESTERS

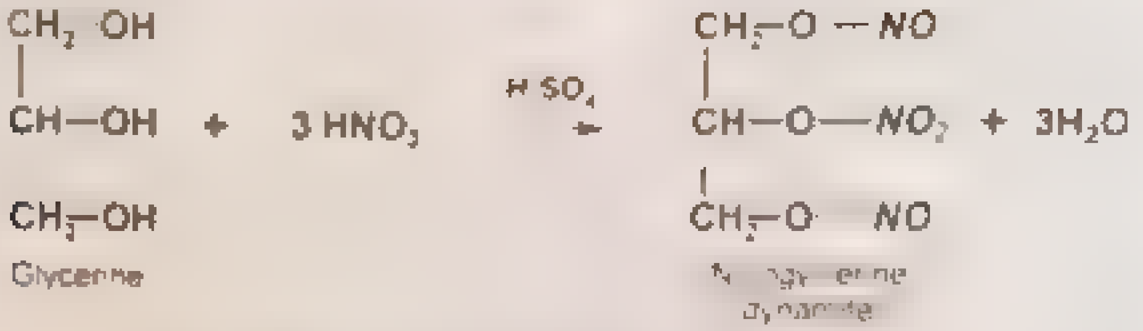
- Alcohols react with organic as well as inorganic acid to form their respe[illegible]

$$CH_3COOH + C_2H_5OH \rightarrow CH_3COOC_2H_5 + H_2O$$

- Thus alkyl halides may also be called esters of halogen acids

$$ROH + HX \rightarrow RX + H_2O$$

- Glycerine ... or Glycerol ...



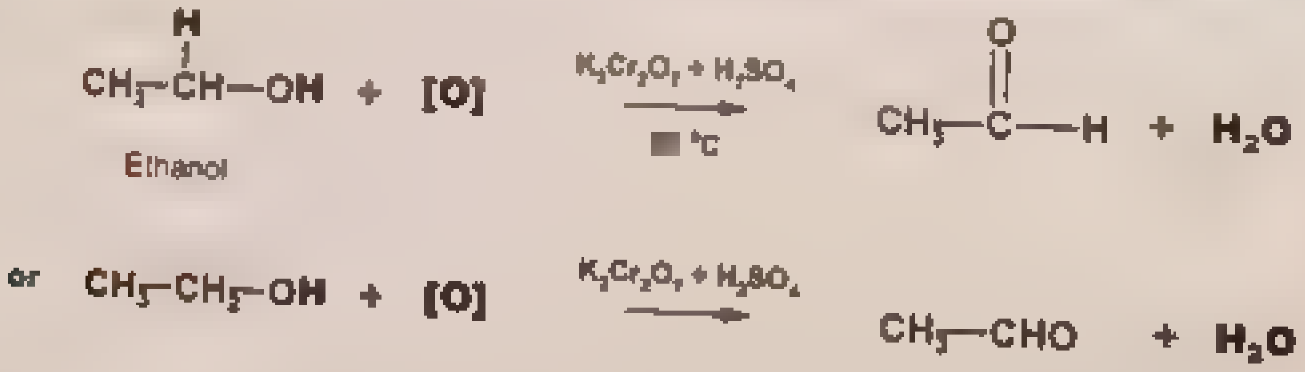
- Nitroglycerine is highly ... and moulded into sticks ... Dynamite
- Esters are also formed by treating ...

(5) OXIDATION

Alcohols are easily oxidized by alkaline $KMnO_4$ or $K_2Cr_2O_7 + H_2SO_4$ solutions to give different products

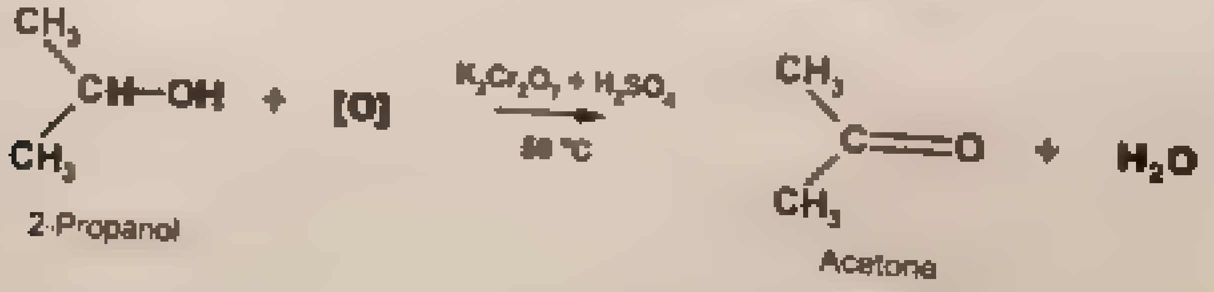
(i) Primary Alcohol:

A primary alcohol is first oxidized to an aldehyde which is further oxidized to a carboxylic acid



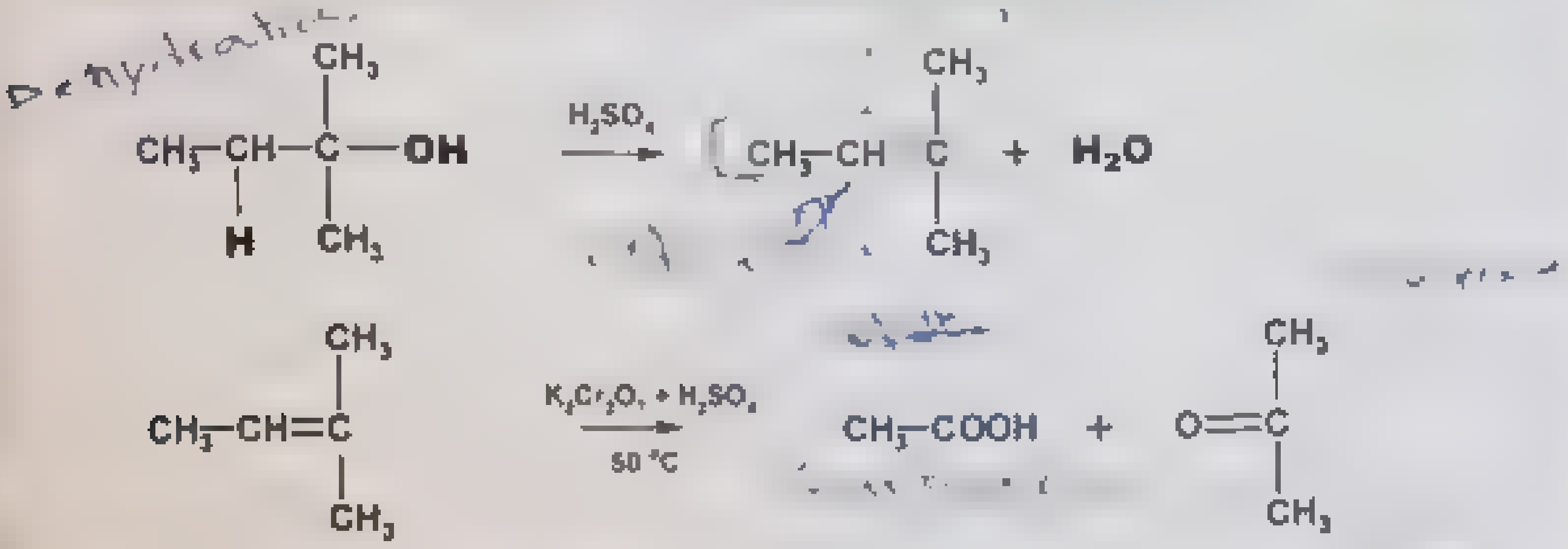
(ii) Secondary Alcohol

A secondary alcohol is oxidized to give a ketone which is not further oxidized



(iii) Tertiary Alcohol

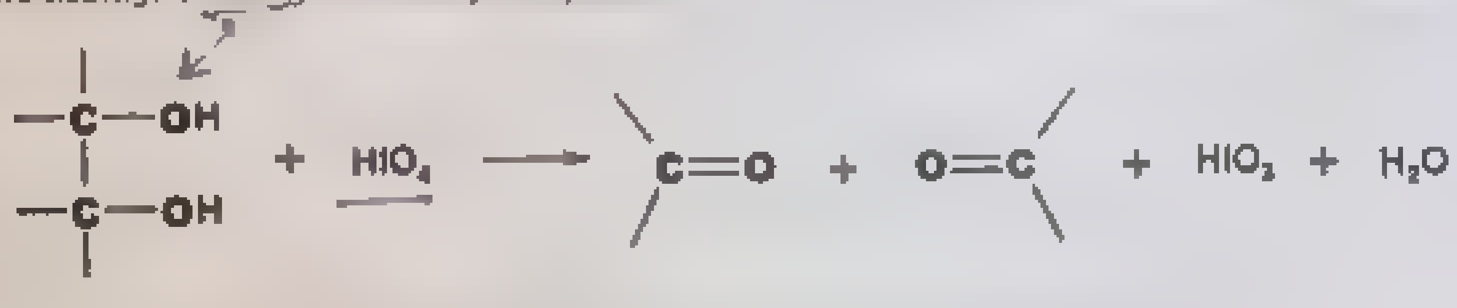
- A tertiary alcohol is not oxidized by alkaline $KMnO_4$
- When heated with a mixture of $K_2Cr_2O_7$ and H_2SO_4 it is first dehydrated to an alkene in the presence of acid. Then alkene is oxidized to a ketone and a carboxylic acid by $K_2Cr_2O_7$ and H_2SO_4



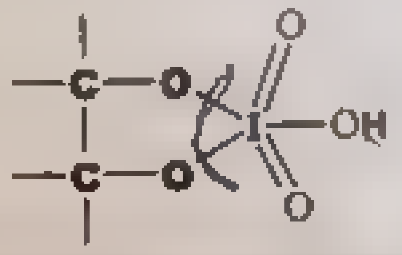
- Thus, each of the products contains lesser number of carbon atoms than the parent alcohol molecule

(6) CLEAVAGE OF 1,2-DIOLS

Oxidative cleavage of diols gives carbonyl compounds



- 1,2- or vicinal diols are cleaved by periodic acid HIO_4, into two carbonyl compounds
- The reaction is selective for 1,2-diols
- This can be used as a functional group test for 1,2-diols.
- The products are determined by the substituents on the diol
- The reaction occurs via the formation of a cyclic periodate ester



THE SULFUR ANALOGUES (THIOLS, RSH)

NOMENCLATURE

- Thiols are the sulfur analogues of alcohols.
- These are names by adding the suffix **–thiol** to the name of corresponding alkanes

CH_3-SH	CH_3-CH_2-SH	$\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-SH$
Methanethiol	Ethanethiol	1-Propanethiol

- The rest of nomenclature (i.e. naming substituents etc.) is similar to alcohols

PHYSICAL PROPERTIES

-
-

STRUCTURE

-
- ... S ... ed to a C atom and a H at ...
- The S-H bonds is less polar than ... is to S are longer and weaker than ...

REACTIVITY

- Thiols are ...
- Thiols are also ...
- Thiols are readily oxidized but to S-O systems rather ... C=S ...
- Thiols are commonly oxidized to disulfides, R-S-S-R ...

QUICK QUIZ-1

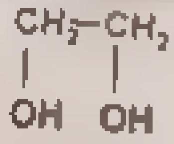
(1) What are monohydric and polyhydric alcohols?

Monohydric alcohols. *Alcohols containing one -OH group are called monohydric alcohols.*

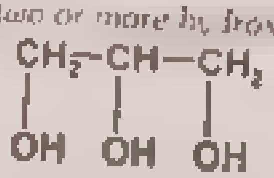
e.g. CH_3-OH Methanol CH_3-CH_2-OH Ethanol

Polyhydric alcohols. *The alcohols containing two or more hydroxy groups are known as polyhydric ...*

e.g.



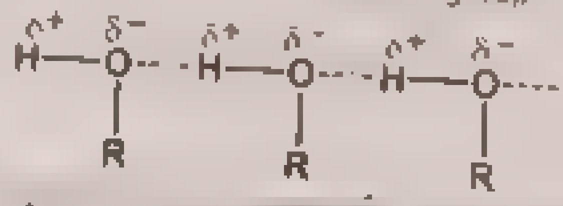
1,2-Ethanediol



1,2,3-Propanetriol

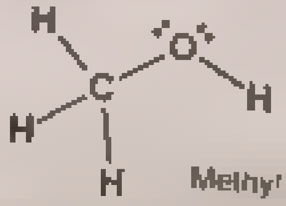
(2) Why some alcohols are readily soluble in water

Small alcohols, e.g. methanol and ethanol are readily soluble in water.
The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but decrease higher alcohol due to increase in non polar nature of alkyl (R) group.



(3) Write the structures of water and methyl alcohol.

Water



Methyl alcohol

(4) Write the formulas of primary, secondary and tertiary alcohols

Primary alcohols. In these, carbon atom attached to OH group is directly attached to one or no carbon atom.

R—OH

Primary alcohol

e.g. CH_3-CH_2-OH

Ethanol

(5) How Grignard's reagent is used for the preparation of alcohols

Page

(6) Define deprotonation

The removal of a proton (H⁺) from molecule or an ion, forming its conjugate ...

$$2ROH + 2Na \longrightarrow \overset{-}{RO}\overset{+}{Na} \quad H_2$$

Sodium alkoxide

The alkoxide ion (RO^-) is the conjugate base of alcohol (**ROH**)

(7) What is a reagent?

A reagent is a compound or a mixture that is added to a system to cause a chemical reaction or test if a reaction occurs

e.g. Baeyer's reagent is dilute solution of $KMnO_4$. It is used to test the presence of a double bond. It reacts with a double bond to form a glycol

PHENOLS

INTRODUCTION

Aromatic compounds containing one or more OH groups, directly attached with carbon of benzene ring, are called phenols.

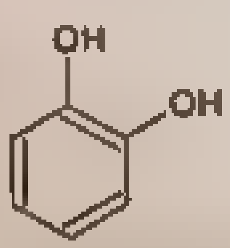
- The simplest example phenol is also known as carbolic acid i.e. C_6H_5OH. It was first obtained from tar by Runge in 1834
- Phenol is derived from the old name for benzene (**phene**) and a suffix (**ol**) is added to it that indicates the presence of hydroxyl group
- Brief information about phenol
  First prepared by Runge. Melting point = 41°C Boiling point = 182°C
  Simplest example of phenol is Carbolic acid (C_6H_5OH)
- Phenols can be obtained via **substitution** reactions, with the hydrolysis of diazonium salts being the most important laboratory method
- Phenols are acidic and are important intermediates in the preparation of aryl ethers C_6H_5-**OR**

NOTE: *The word **phenol (C_6H_5-OH)** is often confused with **phenyl (C_6H_5-)***

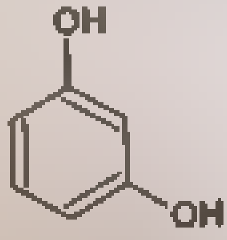
NOMENCLATURE

In common system alcohols are named by adding the word alcohol after the name of the alkyl group to which the –OH group is attached

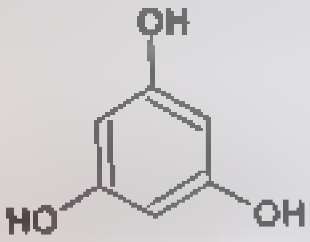
Phenol



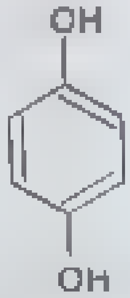
1,2-Dihydroxybenzene (o-Hydroxyphenol) (Catechol)



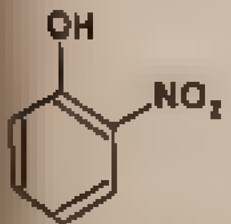
1,3-Dihydroxybenzene (m-Hydroxyphenol) (Resorcinol)



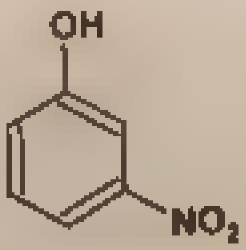
1,2,3-Trihydroxybenzene



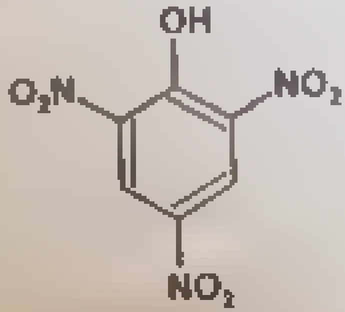
1,4-Dihydroxybenzene (p-Hydroxyphenol) (Hydroquinone)



2-Nitrophenol (o-Nitrophenol)



3-Nitrophenol (m-Nitrophenol)



2,4,6-Trinitrophenol (Picric acid)

STRUCTURE:

- [illegible] atom bonded to an sp^2 hybrid [illegible] phenols
- [illegible] the high [illegible] of [illegible]
- [illegible] exists between [illegible] unshared electron pair on the oxygen and the aromatic ring [illegible] phenol shows following properties
  - [illegible] distance
  - [illegible] oxygen
  - [illegible] proton [illegible]

PHYSICAL PROPERTIES:

(i) Phenol is a [illegible] crystalline poisonous solid with characteristic phenolic odor having melting point 41°C and boiling point 182°C

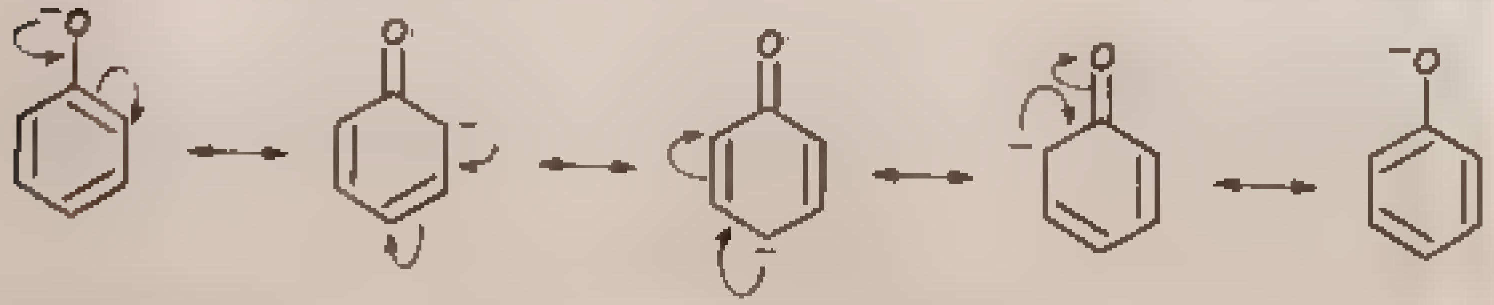
(ii) It is sparingly soluble in water forming pink solution at room temperature but completely soluble above 68.5°C.

(iii) It is poisonous and causes blisters on the skin

ACIDITY:

- Phenols are more acidic (pK_a = 10) than alcohols (pK_a 16 – 20) but less acidic than carboxylic [illegible] (pK_a 5)
- Phenol ionizes in water as

- The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization [illegible] the benzene ring as shown below



- The acidity difference means that it is possible to separate phenols from alcohols and/or carboxylic acids. *When an ether solution of either phenol and alcohol or phenol and carboxylic acid is mixed with dilute base (sodium hydroxide and sodium bicarbonate respectively), then the stronger [illegible] converted into its alkali salt. This salt is extracted to the aqueous phase and can be separated from organic phase.*
- Nucleophilic substitution reactions of phenols are generally carried out under basic conditions as **phenolate ion** is a better nucleophile.

SUBSTITUENT EFFECTS ON ACIDITY

- S[illegible] inductive effects
  The [illegible]
- E[illegible]
- E[illegible]

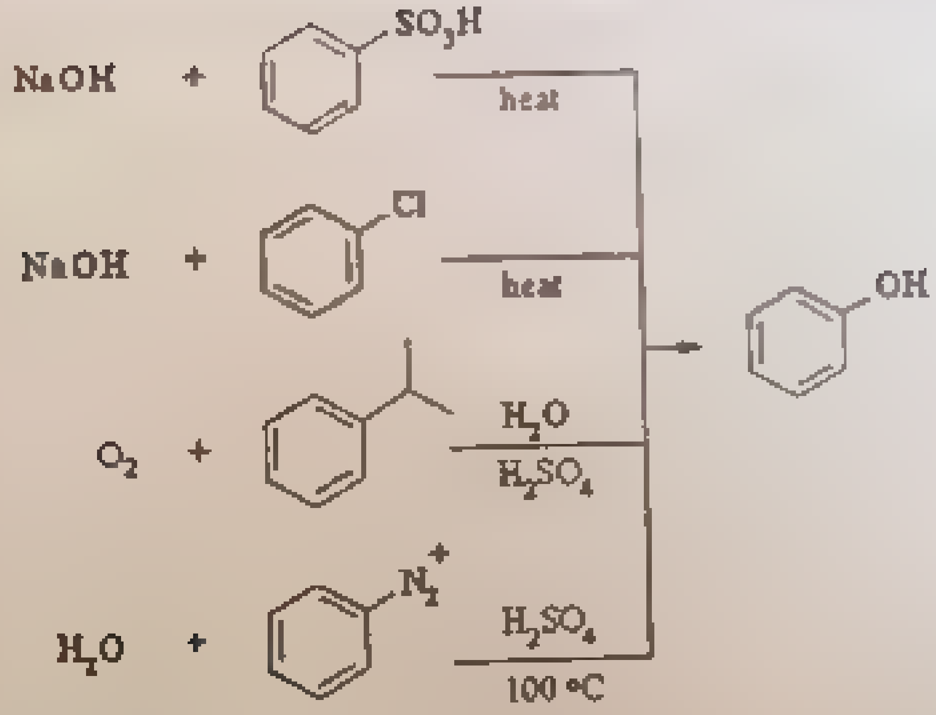
e.g. The [illegible]

:arbonyl
trap

Compound	pKa	Compound	pKa
Phenol	[illegible]		
o-Methoxyphenol	10.0	p-Methoxyphenol	10.2
o-Methylphenol	10.3	p-Methylphenol	10.3
o-Chlorophenol	8.6	[illegible]	[illegible]

PREPARATIONS OF PHENOLS

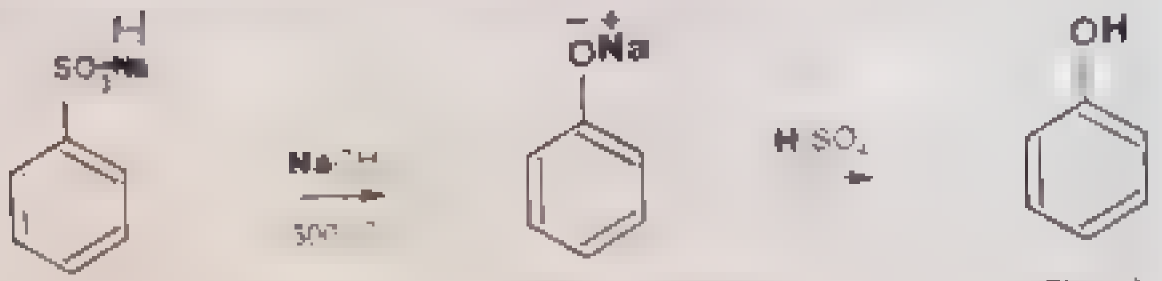
Summary:



NOTE

- The first three methods are primarily industrial methods.
- The hydrolysis of diazonium salts is the most important laboratory method

1) REACTION OF BENZENE SULFONIC ACID WITH HYDROXIDE

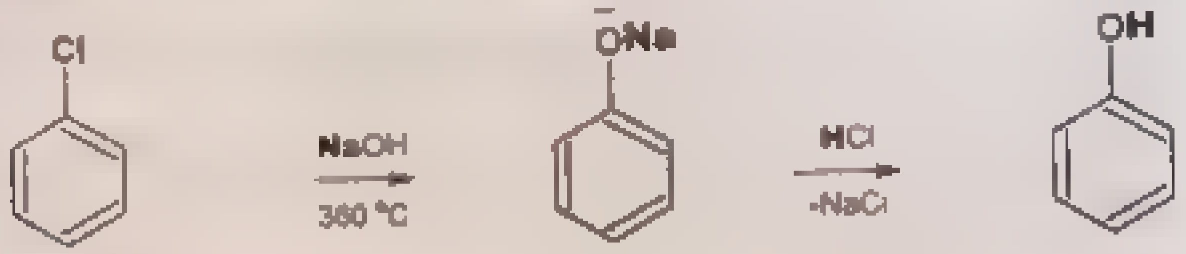


Sodium benzenesulphonate Sodium phenoxide Phenol

- At such a high temperature side reactions also occur

2) BASE HYDROLYSIS OF CHLOROBENZENE

Chlorobenzene is hydrolyzed by heating with NaOH at 360°C and under high pressure



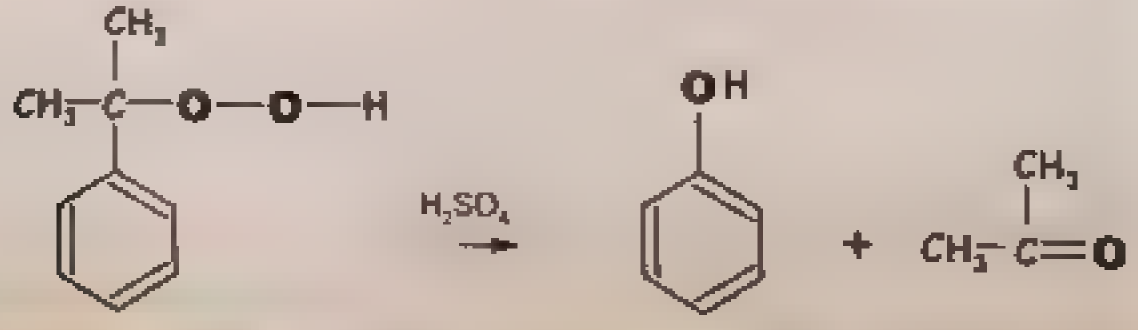
Chlorobenzene

3) ACIDIC OXIDATION OF CUMENE

- It is recently developed commercial method for the preparation of phenol
- Cumene is oxidized by atmospheric oxygen in presence of metal catalyst into cumene hydroperoxide

Isopropylbenzene (Cumene) Isopropylbenzene hydroperoxide

- The hydroperoxide is converted into phenol through an acid catalyzed rearrangement



(i) PREPARATION OF PHENOLS FROM ARYL DIAZONIUM SALTS

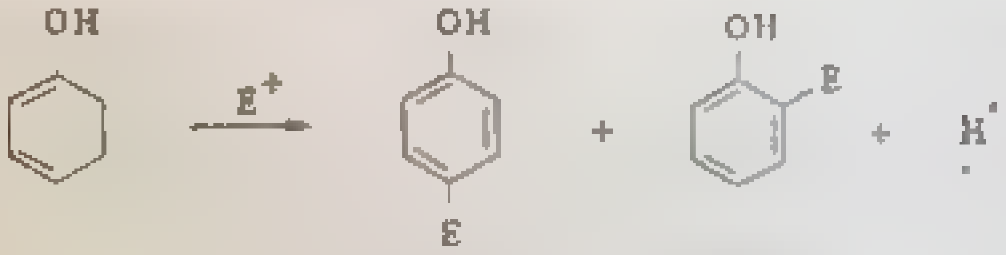
- Aryl diazonium salts can be converted into phenols using aq H_2O, H_2SO_4 [illegible]
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid HNO_2 [illegible]

REACTIVITY:

- Phenols are very react[illegible]
- The OH group is an ortho- para- director therefore it produces ortho- para- products.
- The OH group is an electron donating group and it donates electrons to the ben[illegible] activates the ring. Hence, mild conditions are needed for phenol than that for benzene.

REACTIONS OF PHENOLS

- Phenols are very reactive tow[illegible]
- It is because the hydroxy group (OH) is a s[illegible]



para

- Substitution typically occurs para to the hydroxy group [illegible] substitution occurs.
- The strong activation by OH group means that milder reaction c[illegible] for benzene.
- Phenols are so activated that polysubstitution can occur. The [illegible]

Reaction	Phenol	Benzene
Nitration	dil. HNO_3 in H_2O or CH_3COOH	HNO_3, H_2SO_4
Sulfonation	conc. H_2SO_4	H_2SO_4 + SO_3 [illegible]
Halogenation	X_2	X_2, Fe or FeX_3
Alkylation	ROH, H^+ or RCl, $AlCl_3$	RCl, $AlCl_3$
Acylation	RCOCl, $AlCl_3$	RCOCl, $AlCl_3$
Nitrosation	aq. $NaNO_2$, H^+	

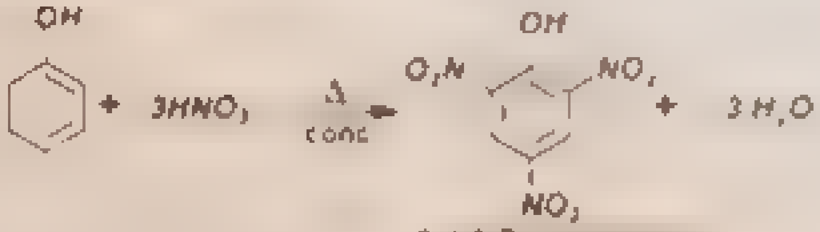
Some of these reactions are given on next page

SOME USEFUL ELECTROPHILIC SUBSTITUTION REACTIONS OF PHENOL

NITRATION

Phenol reacts with d[illegible]

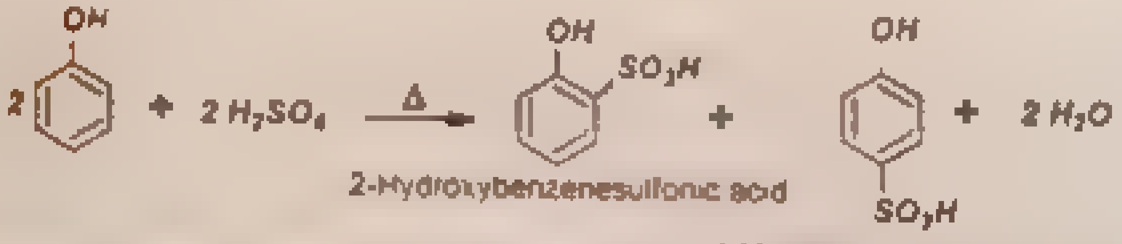
Phenol reacts with [illegible]



2,4,6-T[illegible]
(Picric acid)

SULPHONATION

- Phenol reacts with conc. H_2SO_4 at room temperature to give o- and p-hydroxybenzenesulphonic acids.
- At 20°C o-isomer is formed in greater percentage while at [illegible] p-isomer is formed in greater percentage.



2-Hydroxybenzenesulfonic acid
4-Hydroxybenzenesulfonic acid

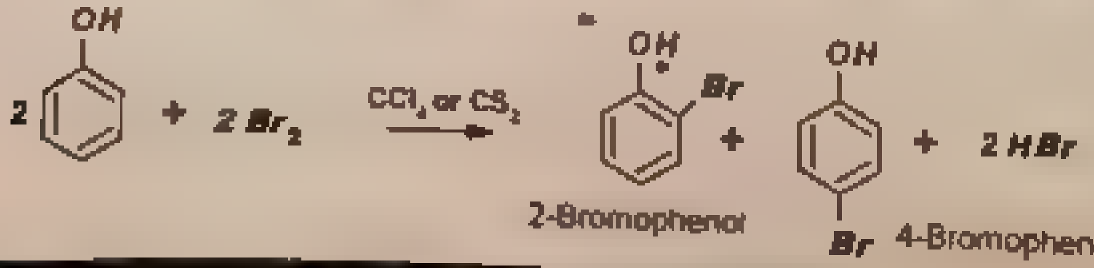
HALOGENATION

No Acid given ?

- Aqueous solution of phenol reacts with bromine water to give white precipitates of 2,4,6-tribromophenol. This test is used for identification of phenol.

2,4,6-Tribromophenol

- When Br_2 is reacted in anhydrous solvent like CS_2, a mixture of o- and p-bromophenols is produced.

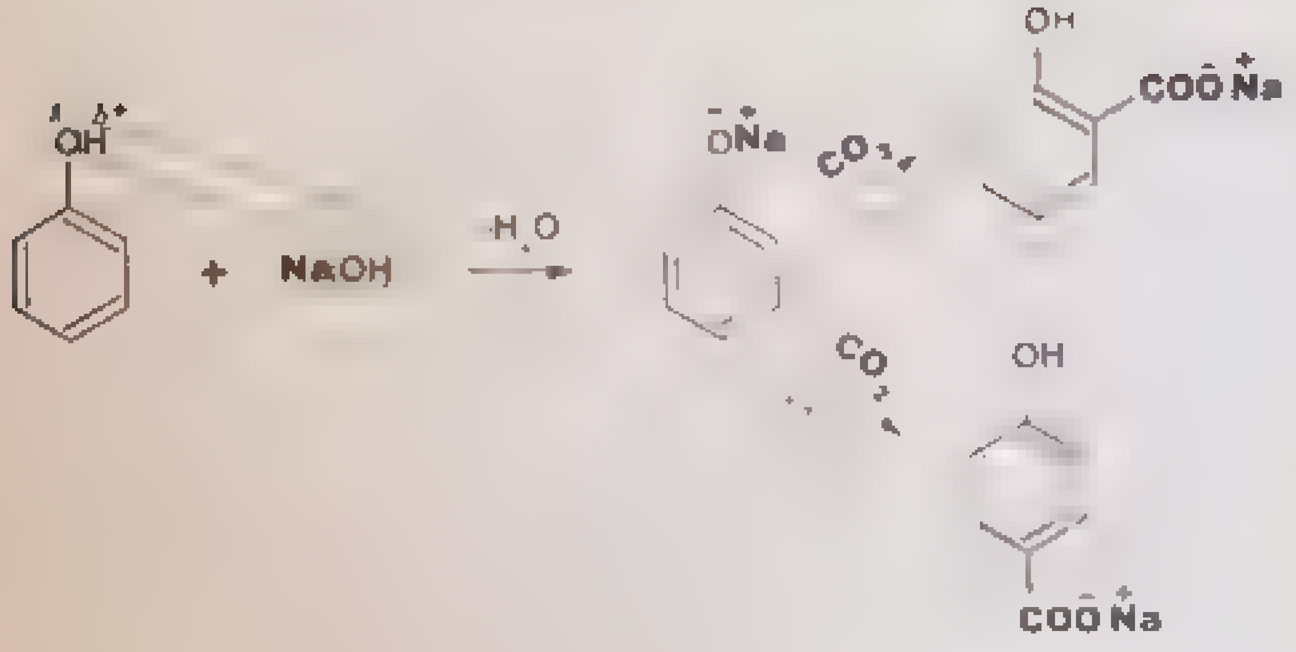


2-Bromophenol
4-Bromophenol

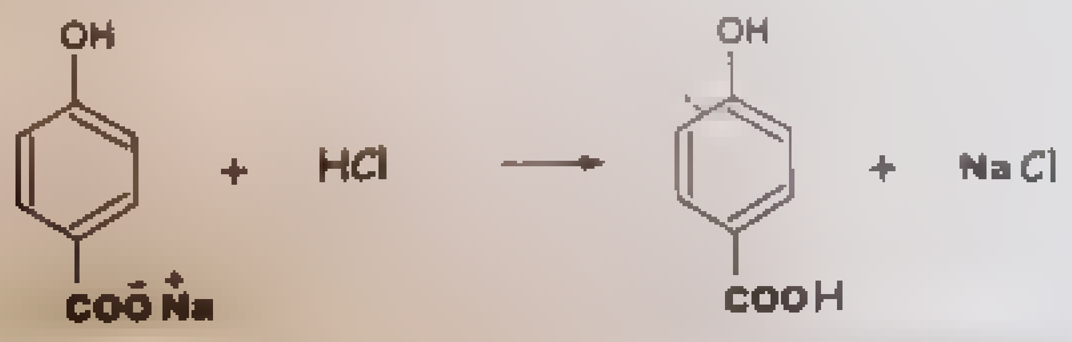
(1) REACTION WITH SODIUM METAL: CARBOXYLATION OF PHENOLS (KOLBE-SCHMITT REACTION)

Quick Quiz-2 4 Explain carbonation of phenols

- The reaction of sodium ...
- At low temperature ... o-product isomerizes ...



- Carbon of CO_2 acts as electrophilic centre in this reaction. Acidification ... corresponding hydroxyl acid.



(2) Oxidation of Phenols

- Phenols are very reactive towards oxidizing agents
- The oxidation takes place through several steps which finally destroys the ring

DIFFERENCE BETWEEN ALCOHOLS AND PHENOL

The main difference between alcohols and phenols are as follows

—ve acidic

Alcohol:

- The compounds in which hydroxyl group is attached to an alkyl group
- Alcohols are hydroxyl derivatives of alkanes
- The compounds in which one hydrogen of water is replaced by an alkyl group
- The general formula of alcohol is R-OH
- Alcohols may be monohydric and polyhydric
- Lower alcohols are generally colorless liquids
- Alcohols have a characteristic sweet smell and burning taste
- They are readily soluble in water but solubility decreases in higher alcohols
- Alcohol reacts with other reagents in two ways, either in which C-O bond breaks or O-H bond breaks

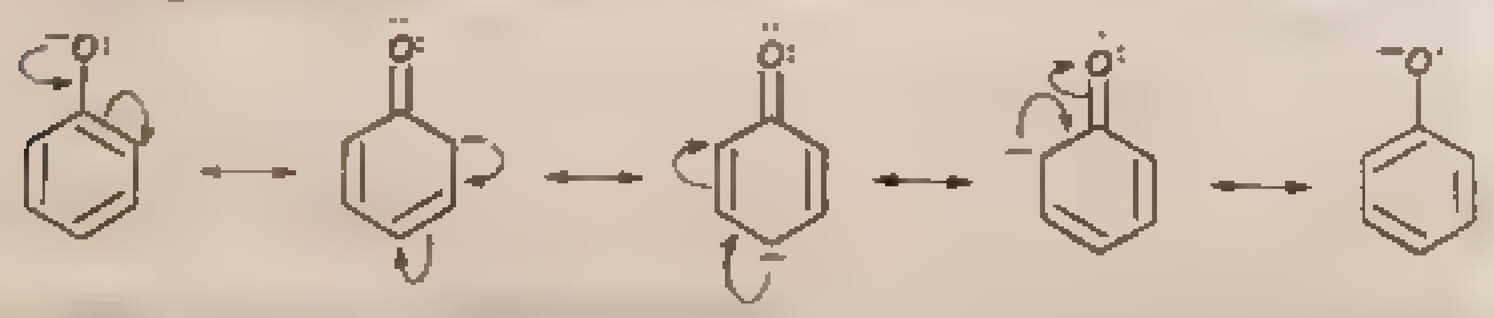
Phenol:

- The compounds in which hydroxyl group is attached to an aryl group
- Phenols are derivatives of benzene
- The compounds in which one hydrogen of water is replaced by an aryl group
- The general formula of phenol is ... It is also known as carbolic acid
- Phenols are not monohydric or polyhydric
- They are colorless, crystalline, deliquescent solids
- They have characteristic phenolic odor
- Its melting point is 41 °C
- Phenols are more acidic ($pK_a = 10$) than alcohols ($pK_a = 16 - 20$)
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble at 68.3 °C
- Phenoxide ions have resonance structures but alcohols don't have such type structures

QUICK QUIZ (2)

(1) How negative charge of phenolate ion is stable?

The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization in benzene ring as shown below:



(2) What is acidity order of phenols

Electron donating groups increases the acidity of phenols while electron withdrawing groups decreases the acidity of phenols

Thus nitrophenols are stronger than phenol while methyl phenols are weaker than phenols

So, with these phenols the order is **(more acidic)** *nitrophenols > phenol > methyl phenol* **(less acidic)**

(3) Why phenols are very reactive towards electrophilic aromatic substitution

- Phenols are very reactive towards electrophilic aromatic substitution
- The OH group is an ortho- para- director therefore it produces ortho- para- products
- The OH group is an electron donating group and it donates electrons to the benzene ring. Thus it activates the ring. Hence mild conditions are needed for phenol than that for benzene

(4) Explain carbonation of phenols

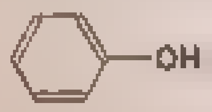
Page

(5) Alcohols and phenols both contain –OH group. What is difference between them?

In alcohols the OH group is directly attached to an alkyl group. Its general formula is R-OH

e.g. $CH_3 - OH$ (Methanol)

In phenols the OH group is directly attached to an aromatic ring. Its general formula is Ar-OH

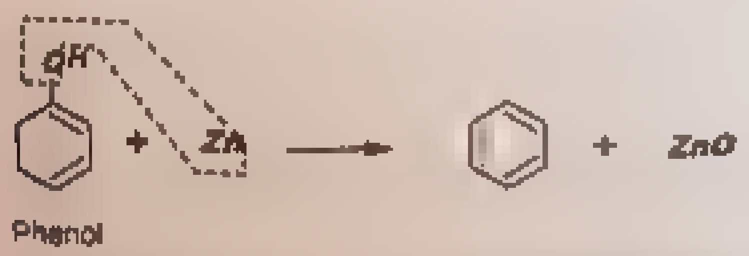
e.g.  phenol

(6) Why phenol is more acidic than ethyl alcohol?

The anion of phenol is stabilized by resonance. The anion of ethyl alcohol cannot be stabilized by resonance. Generally, greater the stability of anion, higher the acidity. So due to greater stability of anion of phenol it is more acidic than ethanol

(7) What happens when phenol is heated with zinc dust

Benzene is obtained by distilling phenol with Zinc dust



(8) What happens when phenol is treated with bromine water?

Aqueous solution of phenol reacts with bromine water to give white precipitates of 2,4,6-tribromophenol. The red colour of bromine water is discharged. This test is used for identification of phenol

2,4,6-Tribromophenol

ETHERS

The compounds in which both hydrogen atoms of water are replaced by alkyl or aryl groups are called ethers

These have general form R R$_2$

Where R and R_2 are alkyl or aryl groups

Ethers are classified into two categories

If $R_1 = R_2$, the ether is called simple or symmetrical ether e g CH_3-O-CH_3

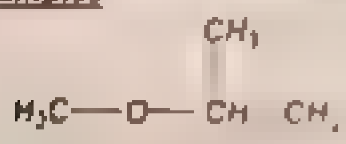
If $R \neq R_2$ the ether is called mixed or unsymmetrical ether e g $CH_3-O\ C_2H_5$

NOMENCLATURE

(i) Common System of Naming

In common system ... names by naming the two groups bonded to oxygen ...

Examples



Methyl iso-propyl ether

$H_3C-O-CH_2-CH_2-CH_3$

Methyl n-propyl ether

$H_5C_2-O-CH_2-CH_2-CH_3$

Ethyl n-propyl ether

$H_3C-CH_2-O-CH_2-CH_3$

Diethyl ether

Exercise Q2 (ix) Write the nomenclature of ether by IUPAC system

(ii) IUPAC System

- In IUPAC system of naming simple ethers are named by naming the two groups linked to oxygen atom followed by the word ether e.g.

$CH_3-CH_2-O-CH_2-CH_3$

Diethyl ether

- Mixed ethers are named as alkyl derivatives of hydrocarbon The smaller alkyl group along with oxygen forms the alkoxy substituent

Examples

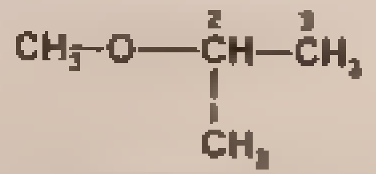
$CH_3-CH_2-O-\overset{1}{C}H_2-\overset{2}{C}H_3$

1-Ethoxyethane

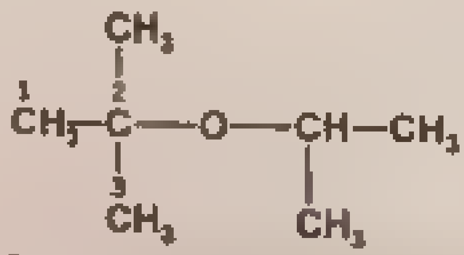
$CH_3-O-\overset{1}{C}H_2-\overset{2}{C}H_2-\overset{3}{C}H_3$

1-Methoxypropane

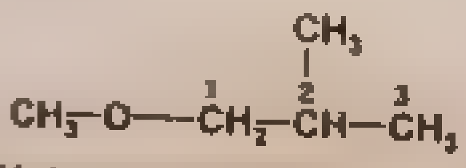
$CH_3OCH(CH_3)CH_3$



2-Methoxypropane



2-iso-Propoxy-2-methylpropane



1-Methoxy-2-methylpropane

PREPARATION OF ETHERS

(1) WILLIAMSON'S SYNTHESIS

$$R-OH + Na + R-X \longrightarrow R-O-R + \ldots$$

(i) $R-OH + Na \longrightarrow R-O^{-}Na^{+} + \ldots$

(ii) $R-O^{-}Na^{+} + R-X \longrightarrow R-O-R + \ldots$

$$CH_3-OH + Na + CH_3-Cl \longrightarrow CH_3-O-CH_3 + NaCl + \ldots H$$

(2) FROM ALKYL HALIDES AND SILVER OXIDE

Alkyl halides are heated with dry silver oxide to form ethers.

$$2\,R-X + Ag_2O \longrightarrow R-O-R + 2\,AgX$$

$$2\,CH_3-CH_2-Cl + Ag_2O \longrightarrow CH_3-CH_2-O-CH_2-CH_3 + 2\,AgCl$$

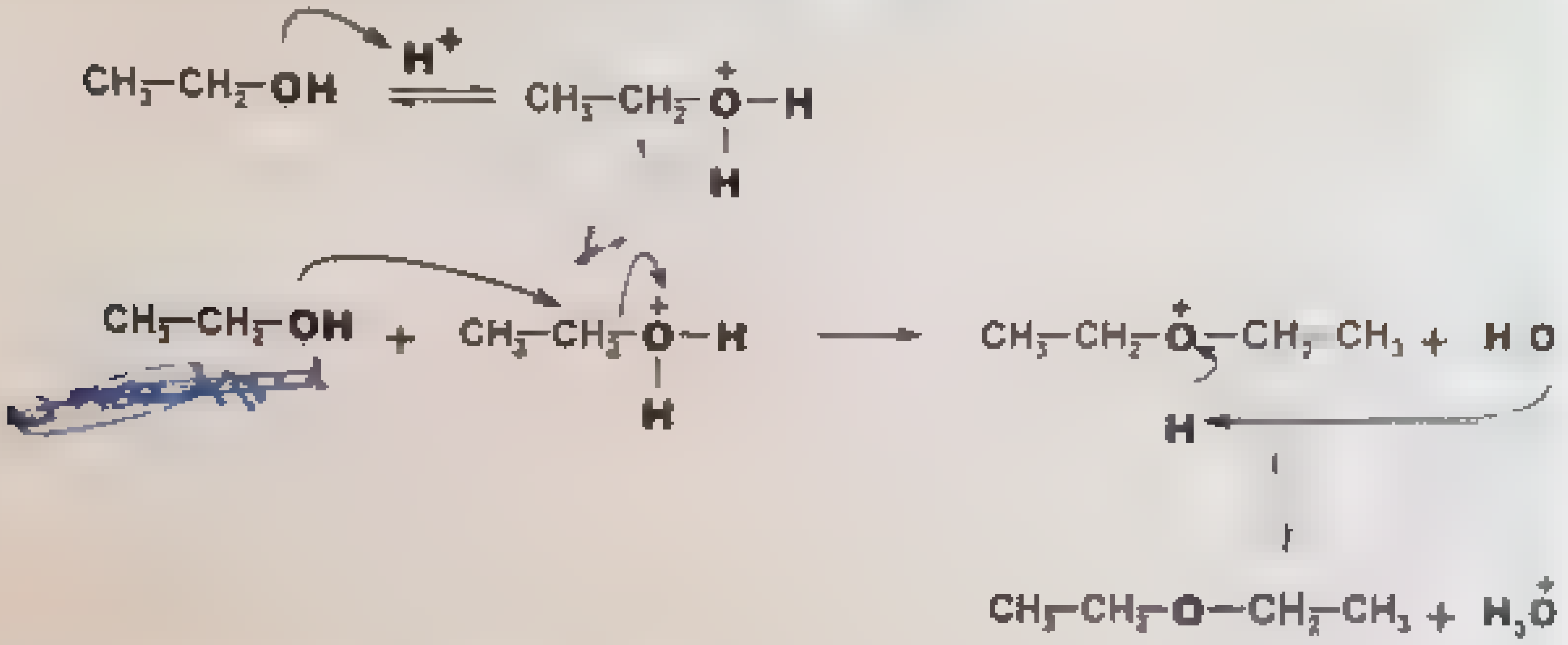
(iii) By Dehydration of Alcohols

By heating excess of alcohol with concentrated H_2SO_4 ...

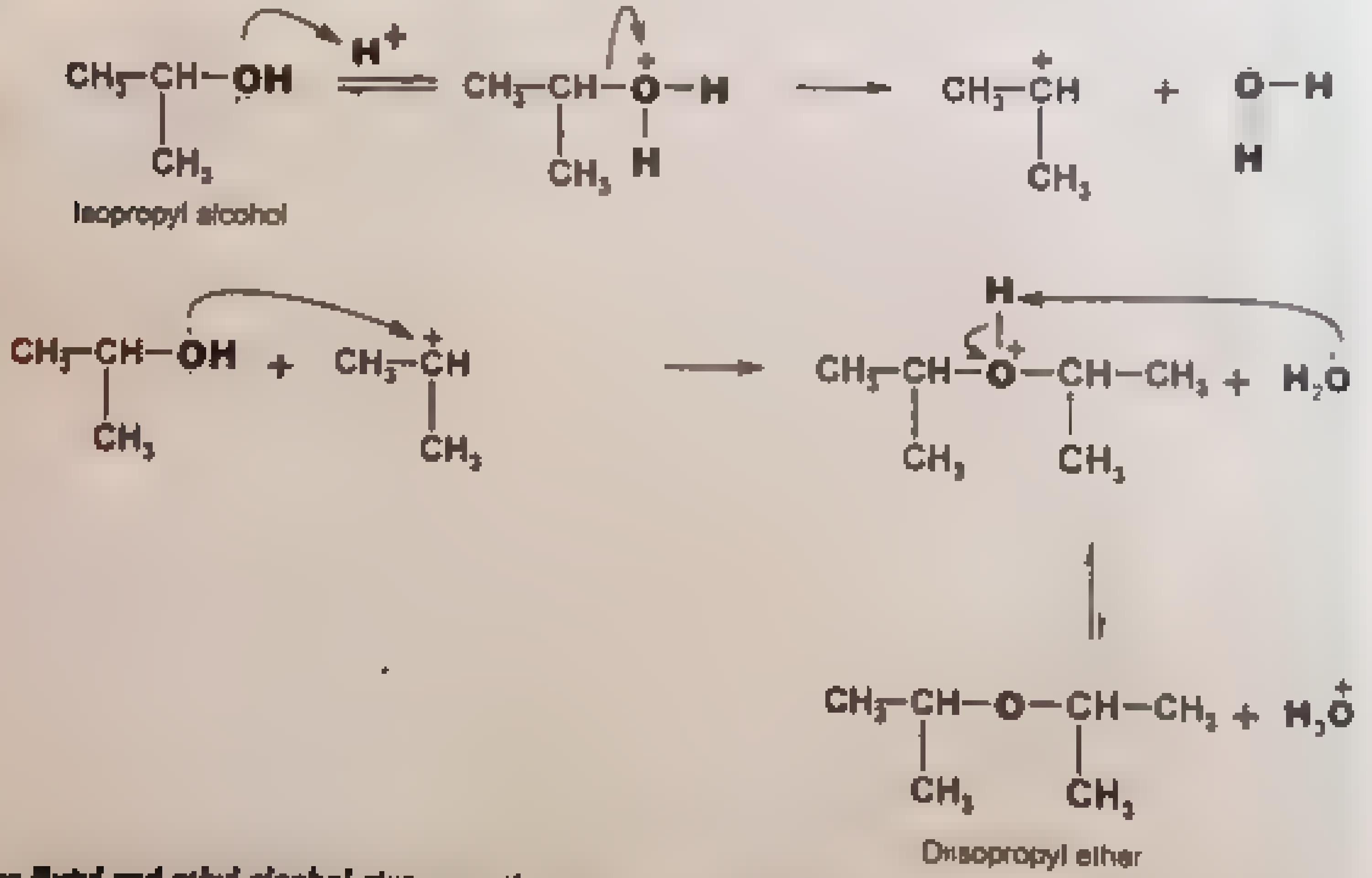
$$2\,CH_3-CH_2-OH \xrightarrow[140^{\circ}C]{\text{conc } H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$$

Diethyl ether

- ***Primary alcohols react through S_N2 mehcanism***



- ***Secondary alcohols react by SN_1-mechanism***



- ***ter-Butyl and ethyl alcohol give one ether.***
- Two different primary alcohols give three ethers when treated with H_2SO_4.

$$CH_3CH_2OH + CH_3OH \rightarrow CH_3OCH_3 + C_2H_5OC_2H_5 + CH_3OOC_2H_5$$

PHYSICAL PROPERTIES

- Ethers are colorless, low boiling, highly inflammable compounds.
- Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compound make them very good solvent
- Ethers are soluble in concentrated sulphuric acid, a characteristic of oxygen containing compounds. This property is used as a test to distinguish between ethers and saturate hydrocarbons

CHEMICAL REACTIVITY:

The image shows the electrostatic potential for dimethyl ether
The more red an area is the higher the electron density and the more **blue** an area is the lower the electron density
The etheral O atom is a region of high electron density (**red**), due to the lone pairs
Ether oxygen atoms are Lewis bases
Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur
The most important reaction of ethers is their cleavage by strong acids such as

(1) RESISTANCE TO OXIDATION:

How ethers show resistance to oxidation?

Ethers are resistant to attack by the usual chemical oxidizing agents. Moreover ... and acids have no action on ethers.

(2) REACTION WITH H-BR

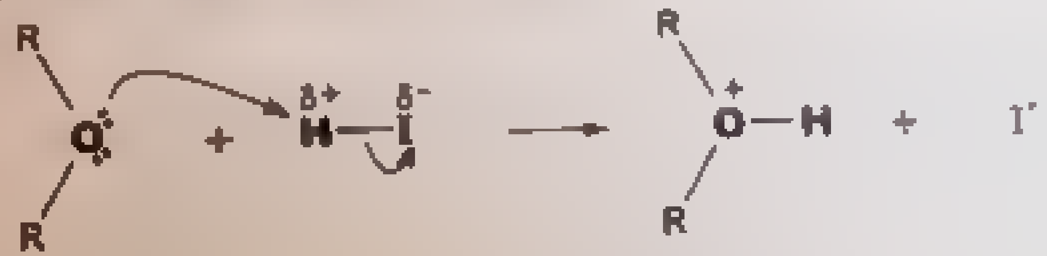
The oxygen atom of an ether molecule possesses unshared electron pairs ... form oxonium ion

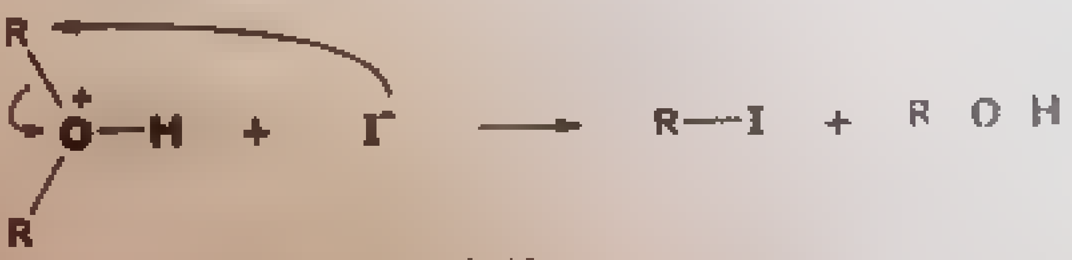
No further reaction takes place.

A species with ... charge on oxygen ...

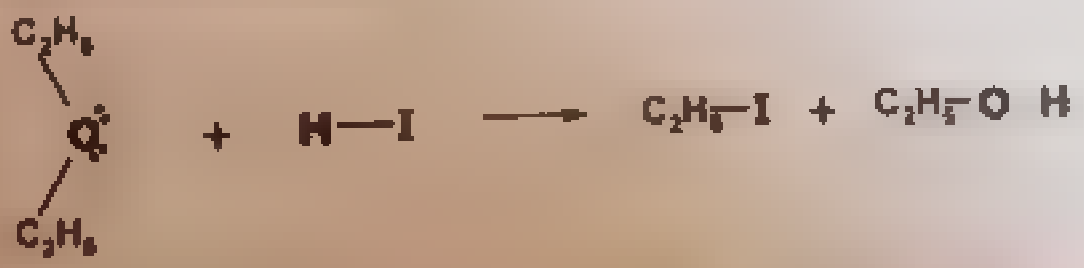
(3) REACTION WITH H-I

The oxygen atom of an ether molecule possesses unshared electron pairs ... form oxonium in, which reacts with I to form R-OH and RI





Diethyl ether reacts with HI to form C_2H_5-OH and C_2H_5I



QUICK QUIZ (3)

(1) How is diethyl ether prepared in the laboratory?

$$C_2H_5-OH + Na \longrightarrow C_2H_5\,\overset{-}{O}\overset{+}{N}a + \tfrac{1}{2}H_2$$

$$C_2H_5\,\overset{-}{O}\overset{+}{N}a + \overset{\delta+}{C_2H_5}-\overset{\delta-}{X} \longrightarrow C_2H_5-O-C_2H_5 + NaX$$

[illegible]

(2) What are symmetrical and unsymmetrical ethers?

The compounds in which both hydrogen [illegible]

These have general form [illegible] groups

(a) If $R_1 = R_2$, the ether is called simple or [illegible]

If $R_1 \neq R_2$, the ether is called mixed or unsymmetrical ether [illegible]

(3) What is Williamson's synthesis? It [illegible]

$$C_2H_5-OH + Na \longrightarrow C_2H_5-\overset{-}{O}\overset{+}{N}a + \tfrac{1}{2}H_2$$

$$C_2H_5\,\overset{-}{O}\overset{+}{N}a + \overset{\delta+}{C_2H_5}-\overset{\delta-}{X} \longrightarrow C_2H_5-O-C_2H_5 + NaX$$

Diethyl ether

SOME IMPORTANT CONVERSIONS

(I) Methanol into ethanol

$$\underset{\text{methanol}}{H_3C-OH} + HCl \xrightarrow{ZnCl_2\,/\,heat} CH_3Cl + H_2O$$

$$2\,CH_3Cl + 2\,Na \xrightarrow{ether} H_3C-CH_3 + 2\,NaCl$$

$$H_3C-CH_3 + Cl_2 \xrightarrow{light} H_3C-CH_2-Cl + HCl$$

$$H_3C-CH_2-Cl + KOH \xrightarrow{aqueous} \underset{\text{ethanol}}{H_3C-CH_2-OH} + KCl$$

(II) Ethanol into methanol

$$\underset{\text{ethanol}}{H_3C-CH_2-OH} + HCl \xrightarrow{ZnCl_2\,/\,heat} H_3C-CH_2-Cl + H_2O$$

$$H_3C-CH_2-Cl + KOH \xrightarrow{aqueous} H_2C=CH_2 + KCl + H_2O$$

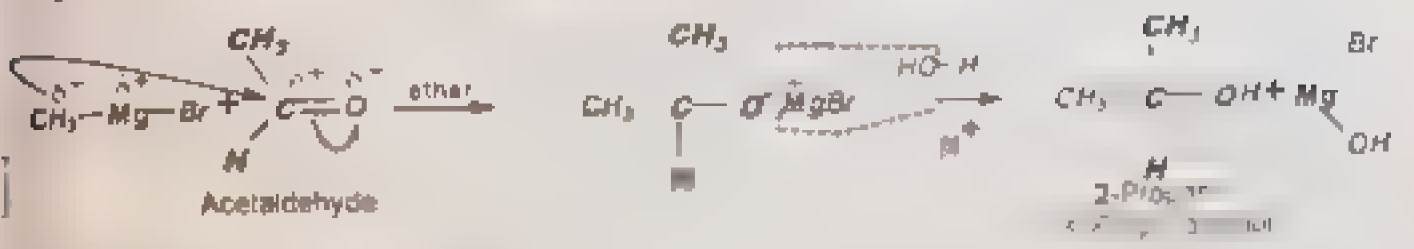
$$H_2C=CH_2 \xrightarrow[ii)\ Zn\,/\,H_2O]{i)\ O_3} 2\ \underset{\text{formaldehyde}}{H-\overset{O}{\overset{\|}{C}}-H}$$

$$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{LiAlH_4} \underset{\text{methanol}}{H_3C-OH}$$

(iii) Ethanol into isopropyl alcohol

$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$$

Ethanol Acetaldehyde



(iv) Ethanol into ethyl methyl ether

$$2\,C_2H_5OH + 2\,Na \longrightarrow 2\,C_2H_5\bar{O}Na^+ + H_2$$

Sodium ethoxide

$$C_2H_5\bar{O}Na^+ + \overset{\delta+}{CH_3}-\overset{\delta-}{Br} \longrightarrow CH_3-OC_2H_5 + NaBr$$

Sodium ethoxide Methyl bromide Methyl ethyl ether

(v) Ethyl alcohol to ethyl iodide

$$CH_3-CH_2-OH + HCl \xrightarrow{ZnCl_2\,/\,heat} CH_3-CH_2-Cl + H_2O$$

ethanol

$$CH_3-CH_2-Cl + NaI \xrightarrow{aqueous} CH_3-CH_2-I + NaCl$$

SOCIETY, TECHNOLOGY AND SCIENCE

1 ANTISEPTICS AND DISINFECTANTS

- Antiseptics and disinfectants are an essential part of infection control practices and aid in the prevention of nosocomial infections.
- They are extensively used in hospitals and other health care settings for a variety of topical and hard surface application.
- A wide variety of active chemical agents or biocides are found in these products many of which have been used for hundred of years for antisepsis disinfection and preservation.
- In general, biocides have a broader spectrum of activity than antibiotics.
- The widespread use of antiseptic and disinfectant products has promoted some speculation on the development of microbial resistance in particular cross-resistance to antibiotics.
- Anti microbial activity of antiseptics and disinfectants can be influenced by many factors e.g. formulation effects, presence of an organic load, temperature, dilution etc.

Antiseptics

An antiseptic is a substance which inhibits the growth and development of micro organisms.

- A antiseptics are thought of as topical agents for application to skin, mucous membrane and inanimate objects. They can be either bactericidal or bacteriostatic.
- Their uses include cleansing of skin and wound, surfaces after injury preparation of skin surface prior to injection or surgical procedure and routine disinfection or surgical procedure and routine disinfection of oral cavity as par of oral hygiene.

Disinfectants

- Disinfectants were [illegible] as [illegible]
- Today disinfectants are widely [illegible] due to [illegible]
- Disinfectants chemi[illegible]

2 ETHER – AN EFFECTIVE ANAESTHETIC

- Before the advent of anaesthetics surgery wa[illegible] surgeons were therefore only [illegible] of a damaged limb that would otherwise b[illegible] could carry out to the present sophisticated form.
- Three of the most important early anae[illegible] N_2O [illegible] (ethoxyethane $CH_3CH_2OCH_2CH_3$) and [illegible] Nitrous oxide is non[illegible] and non flammable but it only prod[illegible] produces deep anaest[illegible] [illegible] damage.

KEY POINTS

- Alcohols are [illegible] derivat[illegible] of aliphatic and [illegible] hydrocarbons
- General formula for alcohol is ROH, for Phenol PhOH, and for ether it is ROR
- Alcohols are usually named by replacing -e [illegible] Alkane with -ol
- Primary [illegible]
- Secondary alcohols can be oxidized to ketones but not further
- Tertiary alcohols [illegible]
- [illegible] atom and a H atom via σ bonds
- [illegible] (pKa = 10) versus ROH (pKa = 16 to 19)
- Phenols are more acidic (pKa = 10) than alcohols (pKa = 16 - 20) but less acidic than carboxylic acids (pKa = [illegible])
- Epoxides are more reactive than simple ethers
- In IUPAC system, ethers are named as alkoxy derivatives of alkanes
- In contrast to alcohol, ethers are fairly unreactive
- Alcohols are soluble in water while phenols are sparingly soluble
- General formula for alcohol is R-OH while for phenol is Ar-OH
- Methyl alcohol has proved to be excellent fuel for racing car
- Ethyl alcohol may be the first organic chemical [illegible] manufactured by humans
- Ethyl alcohol is also named as wine, beer and whiskey
- Fusel oil mainly consists of amyl alcohol ($C_5H_{11}OH$)
- 95% ethyl alcohol is known as rectified spirit or commercial alcohol
- Ethylene glycol is the major component in commercial coolants and anti freeze
- Glycerol is an excellent moisture retaining agent. It is used in vanishing creams, body lotions, shaving foams and tooth pastes
- Bakelite (plastic) is phenol form aldehyde resin
- Phenol is used as starting material for drugs such as salol, aspirin, phenolphthalein and several other dyes
- Diethyl ether has been used in surgery for anaesthesia
- Cyclic ethers are known as epoxides

EXERCISE

Q1: Select the right answer from the choices given with each question.

1. **Which compound shows hydrogen bonding?**
   (a) [illegible] (b) [illegible] (c) [illegible] (d) [illegible]
2. **Which compound is called a universal solvent?**
   (a) H_2O (b) [illegible] (c) [illegible] (d) [illegible]
3. **According to Lewis concept ethers behave as**
   (a) Acid (b) Base (c) Acid as well as base (d) None of them
4. **Ethanol can be converted into ethanoic acid by**
   (a) Hydrogenation (b) [illegible] (c) [illegible] (d) [illegible]
5. **Ethanol is denatured by adding**
   (a) methanol (b) Carbolic acid (c) Acetone (d) Propanol
6. **When phenol reacts with CH_3COCl the product formed is:**
   (a) Ether (b) Alcohol (c) Aldehyde (d) Ester
7. **Williamsons synthesis of ethers is superior to alcohols because it makes**
   (a) Symmetrical ethers (b) Asymmetrical ethers
   (c) Ether at room temperature (d) Both symmetrical and asymmetrical ethers
8. **A methyl phenol is also called**
   (a) A cresol (b) Benzyl alcohol (c) [illegible] (d) [illegible]
9. **Which one of the following compounds does not contain carboxylic group**
   (a) Acetic acid (b) Formic acid (c) Benzoic acid (d) Picric acid
10. **Hydrogen bonding is maximum in**
    (a) Diethyl ether (b) Ethanol (c) Ethyl alcohol (d) Triethyl amine
11. **Which of the following compounds have no attraction at all with water?**
    (a) [illegible] (b) [illegible] (c) [illegible] (d) [illegible]
12. **Phenols are more acidic than alcohols which statement is correct?**
    (a) Phenol turns blue litmus paper red (b) [illegible] liberates CO_2 with carbonate solution
    (c) Phenoxide ion is stabilized due to resonance (d) Alkoxide [illegible]
13. **Carbolic acid is treated with dilute nitric acid at 25°C, the product is**
    (a) o-nitrophenol (b) p-nitrophenol (c) [illegible] (d) [illegible]
14. **Oxonium ion is formed when**
    (a) Ethnol reacts with Na metal (b) Phenol reacts NaOH solution
    (c) Ether is treated with H^+ (d) Ethanol is treated with aq [illegible]
15. **2,4,6-Trinitrophenol is commercially called as**
    (a) TNT (b) Picric acid (c) Carbolic acid (d) [illegible]

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d) C_2H_5OH
C_2H_5OH shows hydrogen bonding, since it contains OH group.

(ii) Ans: (a) H_2O
[illegible]

(iii) Ans: (b) Base
According to Lewis concept, a base is defined as "electron pair Donor" specie. Since ether has lone pairs of electrons on oxygen atom, (R – Ö – R), so it can donate these and thus it can behave as a Lewis base.

(iv) Ans: (c) Oxidation
[illegible] ethanol [illegible] $K_2Cr_2O_7$ [illegible]

(v) Ans: (a) methanol
Methanol is added to ethanol to make it unfit for drinking.

(vi) Ans: (d) Ester
[illegible]

(vii) Ans: (d) Both symmetrical and asymmetrical ethers
Williamsons synthesis uses an alkoxide and an alkyl halide. Thus, both symmetrical and unsymmetrical ethers can be prepared.

(viii) Ans: (a) A cresol

(ix) Ans: (d) Picric acid

(x) Ans: (b) Ethanol or (c) Ethyl alcohol

(xi) Ans: (a) C_6H_6

(xii) Ans: (c) Phenoxide ion is stabilized due to resonance

(xiii) Ans: (d) Both a and b

(xiv) Ans: (c) Ether is treated with HI

(xv) Ans: (b) Picric acid

Q2: Give brief answers for the following questions.

1. What are alcohols? How are they classified?

Monohydric alcohols

Polyhydric alcohols

Alcohol

Classification of Monohydric Alcohols

(i) Primary alcohols

In these

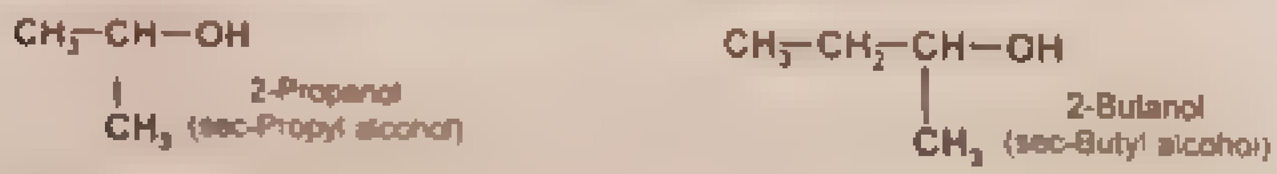
CH_3-OH Methanol

CH_3-CH_2-OH Ethanol

$CH_3-CH_2-CH_2-OH$ 1-Propanol (n-propyl alcohol)

(ii) Secondary alcohols

In these carbon atom attached to OH group is directly attached to two carbon atoms

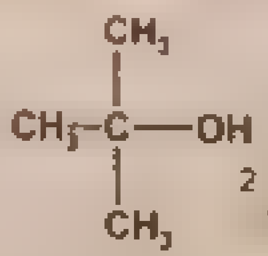


2-Propanol (sec-Propyl alcohol)

2-Butanol (sec-Butyl alcohol)

(iii) Tertiary alcohols

In these carbon atom attached to OH group is directly attached to three carbon atoms



2-Methyl-2-propanol (ter-Butyl alcohol)

(ii) How are monohydric alcohols classified?

Monohydric alcohols are classified into the following three families

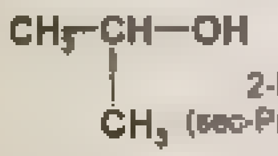
(i) Primary alcohols.
In these, carbon atom attached to OH group, is directly attached to one or two carbon atom

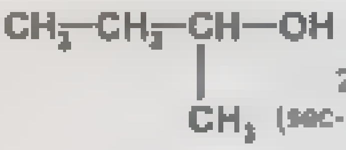
CH_3-OH Methanol

CH_3-CH_2-OH Ethanol

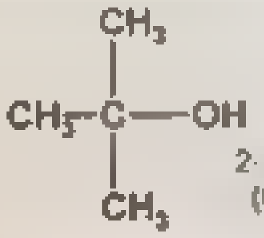
$CH_3-CH_2-CH_2-OH$ 1-Propanol (n-propyl alcohol)

(ii) Secondary alcohols.
In these, carbon atom attached to OH group, is directly attached to two carbon atoms


2-Propanol (sec-Propyl alcohol)


2-Butanol (sec-Butyl alcohol)

(iii) Tertiary alcohols.
In these, carbon atom attached to OH group, is directly attached to three carbon atoms


2-Methyl-2-propanol (ter-Butyl alcohol)

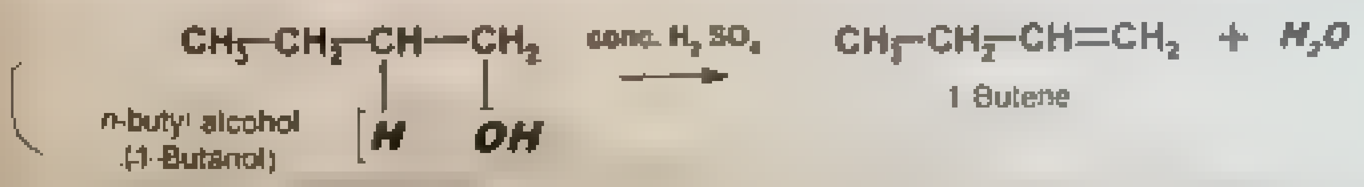
(iii) Compare the acidity of primary, secondary and tertiary alcohols

- Due to the electronegativity of the O atoms, alcohols are slightly acidic
- The anion derived by the deprotonation of an alcohol is the **alkoxide**

$$ROH + H_2O \rightleftharpoons RO^- + H_3O^+$$

- The alkyl groups attached to α-carbon atom decreases the acidity
- Thus, primary alcohol is more acidic than secondary which is more acidic than tertiary alcohols

(iv) 2-Butene is the major product when n-butyl alcohol is heated with conc H_2SO_4. Explain



The stability of alkene increases with increase in degree of substitution on double bond. [illegible] alkylated alkenes are more stable. Since, 1 butene is less alkylated than 2 butene, therefore [illegible] conditions, 1 butene rearranges to 2-butene. Hence, 2-butene is the major product

$$\underset{\substack{\text{1-Butene}\\ (minor)}}{CH_3-CH_2-CH=CH_2} \xrightarrow{\text{Rearrangement}} \underset{\substack{\text{2-Butene}\\ (major)}}{CH_3-CH=CH-CH_3}$$

4. Give the mechanism of dehydration of alcohols

Step: $CH_3-CH_2-OH \xrightleftharpoons{H^+} CH_3-CH_2-\overset{+}{O}-H \longrightarrow CH_3-\overset{+}{C}H_2 + H_2O:$
(with H on the O of the protonated alcohol)

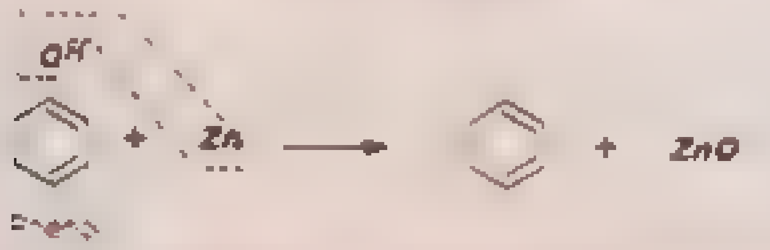
carbocation

Step: $\overset{+}{C}H_2-CH_2-H + H_2O: \longrightarrow CH_2=CH_2 + H_3\overset{+}{O}:$

NOTE: The mechanism for the formation of ethers is given on page 255

(i) How will you obtain benzene from alcohol phenol?

Benzene is obtained by distilling phenol with zinc dust.



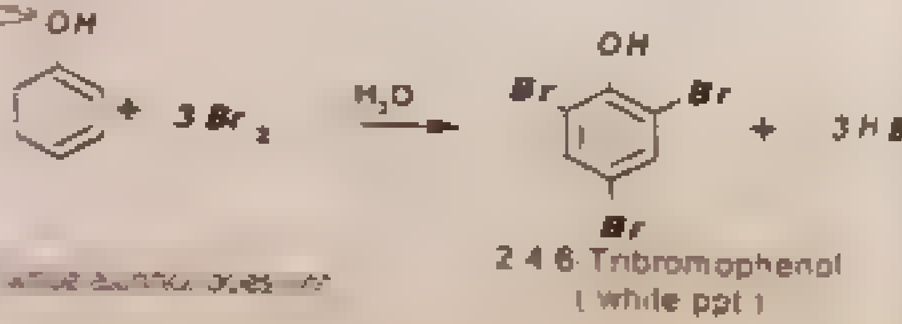
(ii) Alcohols phenols both have OH group but phenols are more acidic than alcohols

Phenols are more acidic than alcohols. This is because the negative charge of phenoxide ion is stabilized by resonance due to delocalization of charge over the ring. In alcohols there is no resonance stabilization of alkoxide ion.

(iii) How will you differentiate between an alcohol and phenol?

These can be distinguished by following ways

- Phenol gives white ppt with Br_2 water while alcohol does not



- Alcohol is neutral while phenol is acidic
- Phenol gives deep purple colour with $FeCl_3$ while alcohol does not

(iv) **Write the nomenclature of ether by IUPAC ...**

See Page 25?

(v) **Why is phenol more soluble in water ...**

Q3: Give detailed answers for the following questions.

1. **How will you prepare alcohols or ...**

INDUSTRIAL PREPARATION OF METHANOL

Me...

200 atmosp...

$$CO + 2H_2 \xrightarrow[450\,^{\circ}C]{} ...$$

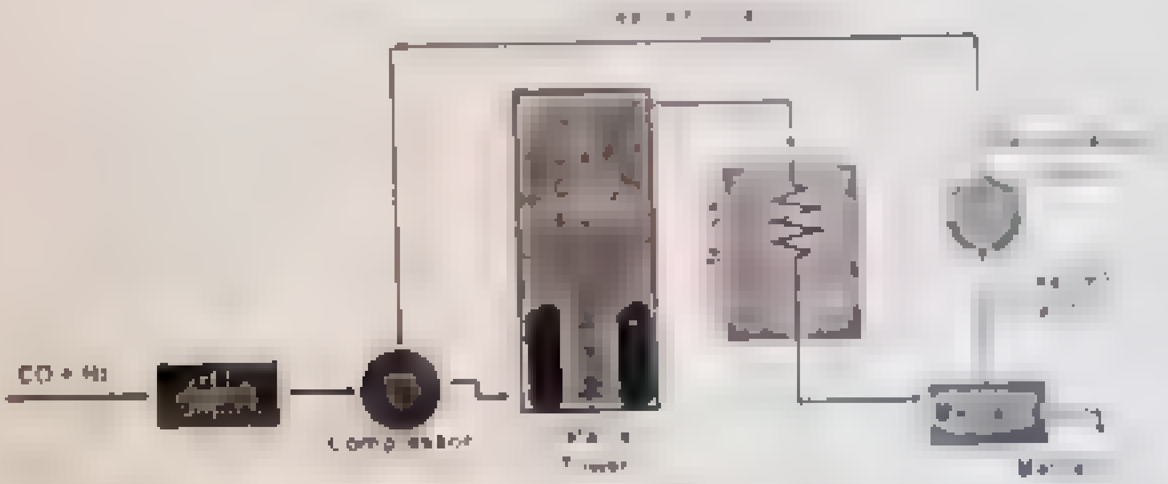


Fig. Flow sheet diagram for the manufacturing of methanol

- In this process, a mixture of CO and H_2 ... to 400 – 500 °C
- These are then taken to the reaction cham...
- CO and H_2 reacts together to give methanol vapour
- These vapours are passed through a condenser ...
- Unreacted gases are recycled through compressor ...

INDUSTRIAL PREPARATION OF ETHANOL

All over the world ethanol is prepared on industrial scale by the process of fermentation.

- Fermentation is a bio-chemical process which occurs in the presence of certain enzymes secreted by micro-organisms such as yeast.
- Optimum temperature for this process is 25-35°C.
- Proper aeration, dilution of solution and absence of any preservative are essential ... for fermentation
- In Pakistan ethanol is prepared by the fermentation of molasses, starch grains or fru...es

From Molasses

The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses

It is fermented by enzymes present in yeast to give ethanol

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{yeast}]{\text{invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} \underset{\text{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2$$

From starch

$$\underset{\text{Starch}}{2\,(C_6H_{10}O_5)n} + n\,H_2O \xrightarrow[\text{yeast}]{\text{diastase}} \underset{\text{Maltose}}{n\,C_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{yeast}]{\text{maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow[\text{yeast}]{\text{zymase}} \underset{\text{Ethanol}}{2\,C_2H_5OH} + 2\,CO_2$$

Collection of Ethanol

- An alcohol obtained by fermentation is only upto 12%
- It never exceeds 14% because above this enzymes become inactive
- This alcohol is distilled again and again to obtain 95% alcohol which is called rectified spirit
- Absolute alcohol is obtained by re-distillation of rectified spirit in the presence of CaO, which absorbs moisture

2. Distinguish ethanol from methanol and ethanol from phenol.

Methanol and Ethanol

These can be distinguished by Iodoform test

Ethanol gives yellow ppt of iodoform on reacting with NaOH and I_2

Methanol does not give yellow ppt of iodoform with NaOH and I_2

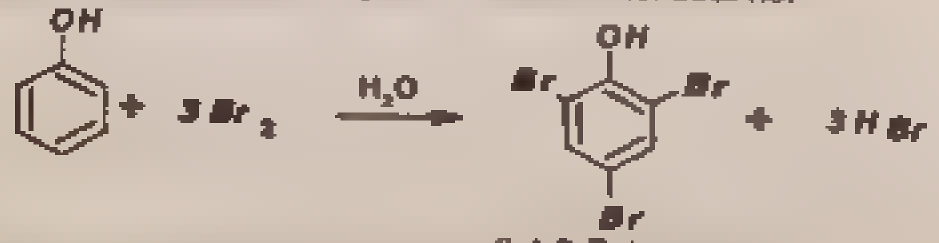
$$C_2H_5OH + 4\,I_2 + 6\,NaOH \longrightarrow \underset{\substack{\text{iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + HCOONa + 5\,NaI + 5\,H_2O$$

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No Yellow ppt}$$

Phenol and Ethanol

These can be distinguished by following ways

- Phenol gives white ppt with Br_2 water while alcohol does not



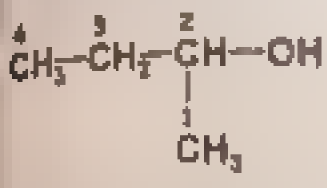
2,4,6-Tribromophenol
(white ppt)

- Alcohol is neutral while phenol is acidic
- Phenol gives deep purple colour with $FeCl_3$ while alcohol does not

3. How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.
See Page 274

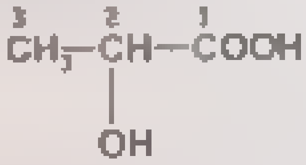
4. Give IUPAC names and structures of the following compounds

(i) sec-Butyl alcohol



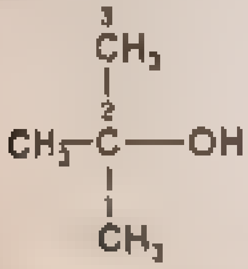
2-Butanol

(ii) Lactic acid



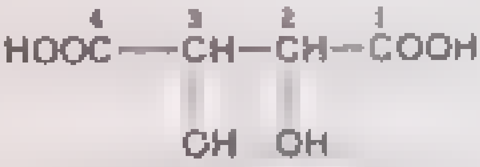
2-Hydroxypropanoic acid

(iii) ter-Butyl alcohol



2-Methyl-2-propanol

(iv) Tartaric acid



2,3-Dihydroxy...

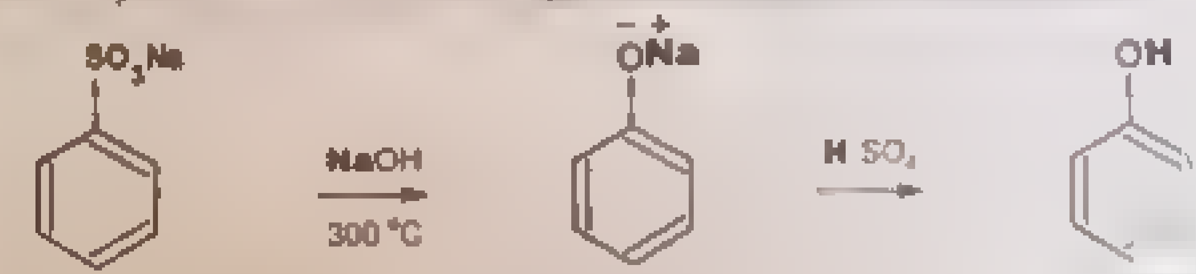
5. Give the reactivity of ethers

- The ethereal O atom is a region of high electron density...
- Ether oxygen atoms are Lewis bases
- Like an alcohol -OH group, the -OR group is a poor leaving group ... needs to be converted ... leaving group before substitution can occur
- The most important reaction of ethers is their cleavage by st... acids such as H... or HBr

6. Give at least two methods for the preparation of phenol

(i) Reaction of Benzene Sulfonic Acid with Hydroxide

Sodium benzene sulphonate on fusion with strong ...

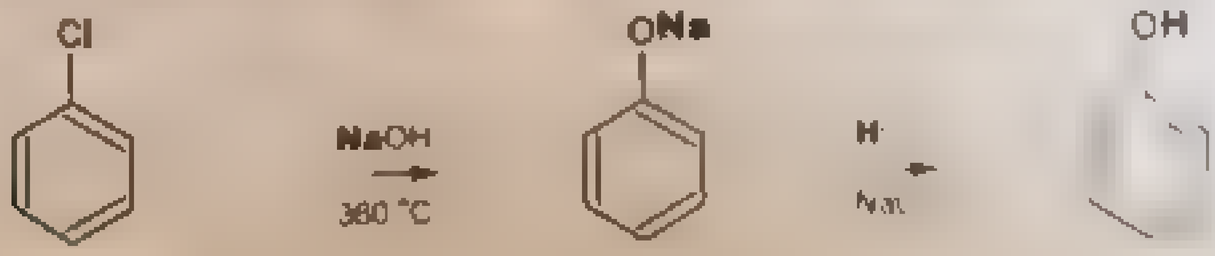


Sodium benzenesulphonate Sodium phenoxide Phe...

- At such a high temperature, side reactions also occur

(ii) Base Hydrolysis of Chlorobenzene

Chlorobenzene is hydrolyzed by heating with NaOH at 360 °C and ...

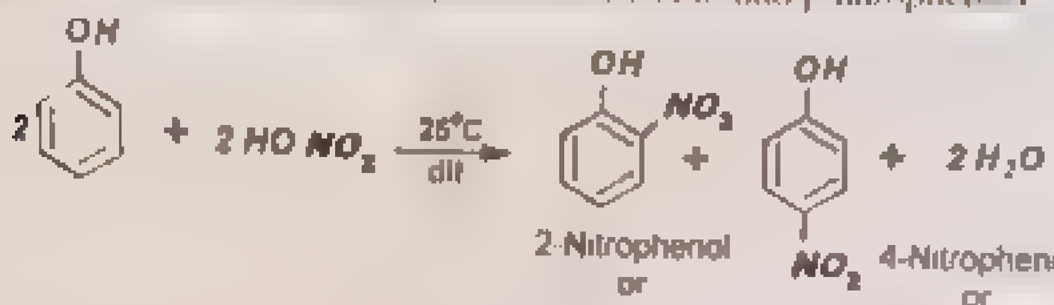


Chlorobenzene

7 How does phenol react with

(i) HNO_3

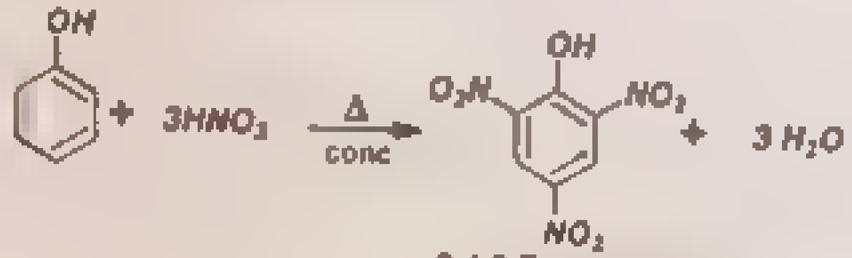
Phenol reacts with dil. HNO_3 to give a mixture of o- and p-nitrophenols



2-Nitrophenol or o-Nitrophenol

4-Nitrophenol or p-Nitrophenol

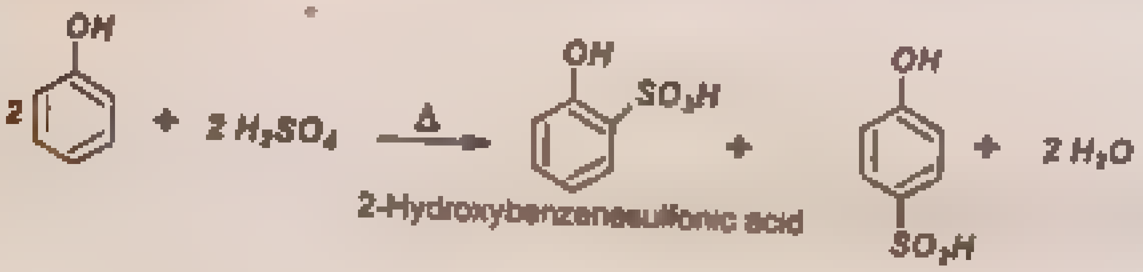
Phenol reacts with conc. HNO_3 to give picric acid



2,4,6-Trinitrophenol
(Picric acid)

(ii) H_2SO_4

- Phenol reacts with conc. H_2SO_4 at room temperature to give o- and p-hydroxybenzenesulphonic acids
- At 20°C o-isomer is formed in greater percentage, while at 100°C, p-isomer is formed in greater percentage

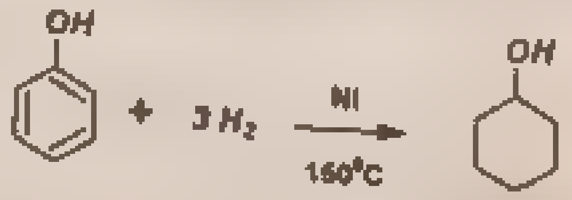


2-Hydroxybenzenesulfonic acid

4-Hydroxybenzenesulfonic acid

(iii) H_2/Pt

When hydrogen is passed through phenol at 150°C in the presence of Ni catalyst it gives cyclohexanol



Cyclohexanol

(iv) NaOH

Phenol reacts with alkalies to form salts, e.g.

Sodium phenoxide

8 What is oxonium ion? Describe the chemical reactivity of ether.

A species with trivalent oxygen and carrying a positive charge on oxygen ... or **oxonium ion**

(For reactivity of ether see Q5)

9 Explain following terms using ethyl alcohol as an example

(i) Oxidation

A primary alcohol is first oxidized to an aldehyde which is further oxidized to a carboxylic acid

$$\underset{\text{Ethanol}}{CH_3-\overset{H}{\overset{|}{C}}H-OH} + [O] \xrightarrow[50\ ^\circ C]{K_2Cr_2O_7 + H_2SO_4} CH_3-\overset{O}{\overset{||}{C}}-H + H_2O$$

$$\text{or}\quad CH_3-CH_2-OH + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} CH_3-CHO + H_2O$$

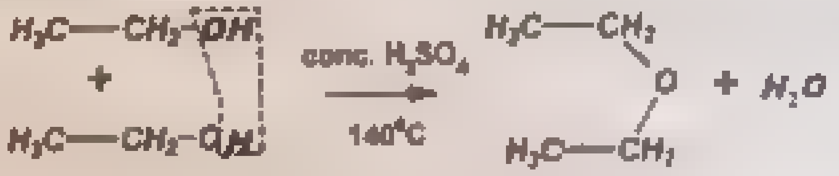
(ii) Dehydration

Alcohols react with conc. H_2SO_4 and give different products at different temperatures

<u>High temperature, low alcohol conc.</u>

$$\underset{H\quad\ OH}{H_2C-CH_2} \xrightarrow[180^\circ C]{conc.\ H_2SO_4} H_2C{=}CH_2 + H_2O$$

<u>Low temperature, high alcohol conc.</u>



Diethyl ether

(iii) Esterification

Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol ...

$$CH_3-\overset{O}{\overset{||}{C}}-OH + C_2H_5-OH \xrightarrow[heat]{H^+} CH_3-\overset{O}{\overset{||}{C}}-O-C_2H_5 + H_2O$$

(iv) Ether formation

Diethyl ether

10 *How does ethyl alcohol react with the following reagents?*

i Conc H_2SO_4

$$\underset{\boxed{H \quad OH}}{H_2C-CH_2} \xrightarrow[180^\circ C]{\text{conc. } H_2SO_4} H_2C=CH_2 + H_2O$$

(ii) Na

$$2\,C_2H_5OH + 2\,Na \longrightarrow \underset{\text{Sodium ethoxide}}{2\,C_2H_5\overset{-}{O}Na^+} + H_2$$

(iii) PCl_5

$$CH_3-CH_2-OH + PCl_5 \longrightarrow CH_3-CH_2-Cl + POCl_3 + HCl$$

(iv) CH_3COOH

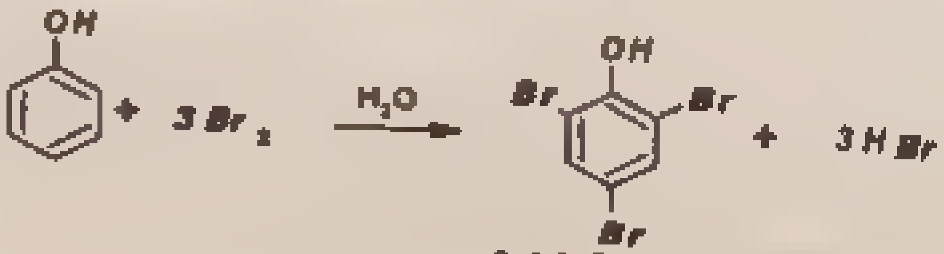
$$CH_3-\overset{O}{\overset{||}{C}}-OH + C_2H_5-OH \xrightarrow[\text{heat}]{H^+} CH_3-\overset{O}{\overset{||}{C}}-O-C_2H_5 + H_2O$$

(v) $SOCl_2$

$$CH_3-CH_2-OH + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{pyridine}} CH_3-CH_2-Cl + SO_2 + HCl$$

11 ***How will you distinguish between?***
(i) **an alcohol and a phenol**
These can be distinguished by following ways

- Alcohol is neutral while phenol is acidic
- Phenol gives white ppt with Br_2 water while alcohol does not.



2,4,6-Tribromophenol
(white ppt)

- Phenol gives deep purple colour with $FeCl_3$ while alcohol does not.

(ii) an alcohol and an ether

These can be distinguished by following test

Alcohols evolve H_2 gas with Na metal while ether does [illegible]

$$2R-OH + 2Na \longrightarrow 2R-O^{-}Na^{+} + H_2$$

(iii) methanol and ethanol

These can be distinguished by [illegible]

Ethanol gives yellow ppt [illegible]

Methanol does not give yellow ppt of [illegible]

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow \underset{\text{[illegible] yellow ppt}}{CHI_3} + HCOONa + 5NaI + 5H_2O$$

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No Yellow ppt}$$

(iv) a tertiary alcohol and a primary alcohol

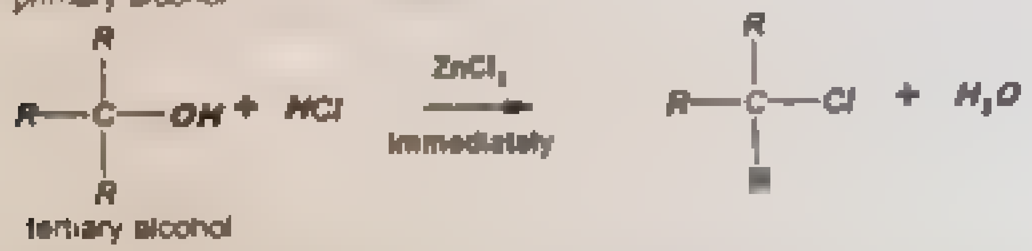
These can be distinguished by Lucas Test

When Lucas reagent ($HCl + ZnCl_2$) is added to an alcohol

Tertiary alcohol forms oily layer of alkyl halide immediately

While primary alcohol forms oily layer only on heating

$$\underset{\text{primary alcohol}}{R-CH_2-OH} + HCl \xrightarrow[\text{heat}]{ZnCl_2} R-CH_2-Cl + H_2O$$



(v) 1-propanol and 2-propanol

1-propanol is primary alcohol while 2-propanol is secondary alcohol. These can be distinguished by Lucas test

When Lucas reagent ($HCl + ZnCl_2$) is added to an alcohol

2-propanol forms oily layer of alkyl halide within 5 – 10 minutes.

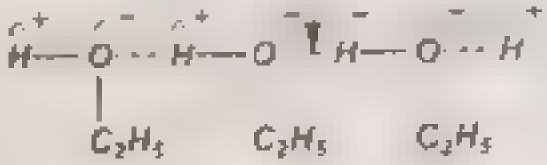
While 1-propanol forms oily layer only on heating

$$\underset{\text{1-propanol}}{H_3C-CH_2-CH_2-OH} + HCl \xrightarrow[\text{heat}]{ZnCl_2} H_3C-CH_2-CH_2-Cl + H_2O$$

12 Give reason for the followings

(i) Ethyl alcohol is a liquid while ethyl chloride is a gas.

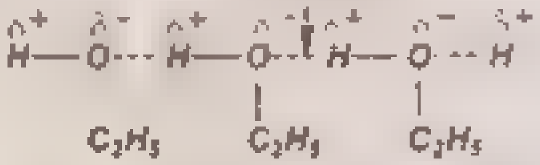
Ethyl chloride has weak dipole-dipole for [illegible]



Due to strong H-bonding in ethanol [illegible] together. Thus ethanol [illegible] while ethyl chloride is gas.

(ii) Ethanol has higher boiling point than diethyl ether

Ethanol has strong hydrogen bonding while diethyl ether [illegible]



Due to strong H bonding in ethanol its molecules are tightly held together. Thus it is d[illegible] ethanol than diethyl ether. Hence ethanol has higher boiling point than diethyl ether.

(iii) Absolute alcohol cannot be prepared by fermentation process

Absolute alcohol can not be obtained by fermentation process. It is because at higher conc. of alc[illegible] enzyme of yeast becomes inactive and process stops.

Actually alcohol obtained by fermentation process is only upto 12 [illegible]. This alcohol is further conce[illegible] by distillation to about 95 % called rectified spirit. Rectified spirit is further distilled with [illegible] absolute alcohol.

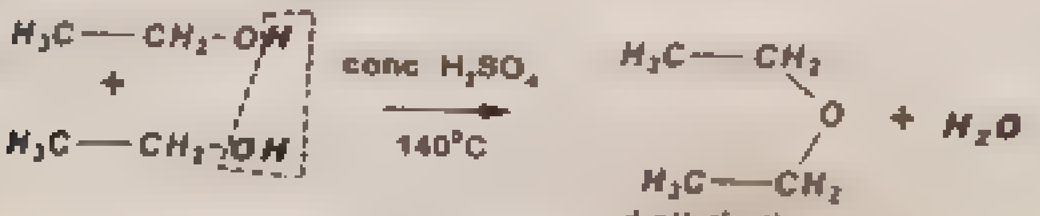
(iv) Ethanol gives different products with conc. H_2SO_4 under different conditions.

Ethanol gives two types of product in different conditions.

High temperature, low alcohol conc.

$$H_3C-CH_2-OH \xrightarrow[180^\circ C]{conc.\ H_2SO_4} H_2C=CH_2 + H_2O$$

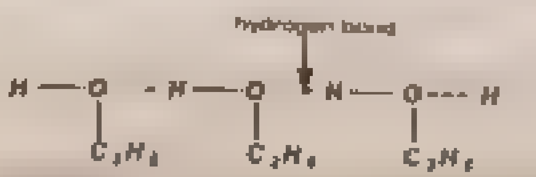
Low temperature, high alcohol conc.

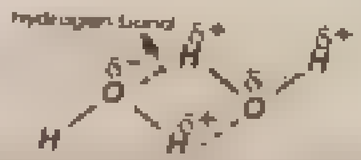


diethyl ether

(v) Water has higher boiling point than ethanol.

In water, two hydrogen bonds are formed per molecule while in ethanol only one hydrogen [illegible] formed per molecule. Thus due to extensive hydrogen bonding in H_2O its boiling point is gre[illegible] ethanol.





EST YOUR SKILLS Marks: 85

OBJECTIVE

Marks: 17

: 20 Minutes

: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Circle the correct option i.e A/B/C/D. Each part carries one mark.

Which one is the general formula for monohydric alcohols?
A. $C_nH_{2n}OH$ B. $C_{n+1}H_{2n+1}OH$ C. $C_{2n}H_{2n+1}OH$ **D. $C_nH_{2n+1}OH$**

Rectified spirit contain alcohol at about
A. 90% B. 100% **C. 95%** D. 85%

Fermentation of starch to give alcohol occurs mainly with the help of
A. O_2 B. Air C. CO_2 **D. Enzymes**

The compound 'B' in the following sequence of reaction is
$CH_3CH_2CH_2OH + PCl_5 \rightarrow A + alc.KOH \rightarrow B$
A. Propyne **B. Propene** C. Propane D. Propanal

Phenol react with acetyl chloride in the presence of a base to form an?
A. Acid B. Alcohol C. Citric acid **D. Ester**

An industrial method for preparation of methanol is
A. **Catalytic reduction of CO + $2H_2$ in the presence of $ZnO.Cr_2O_3$**
B. By reacting methane with steam at 900°C with a Ni-catalyst
C. By reducing HCHO with aqueous NaOH solution
D. By reducing HCHO with $LiAlH_4$ followed by hydrolysis

Ethanol is denatured by adding
A. Methanol B. Acetone C. Propanol **D. All of the above**

Phenol is also known as
A. Carbolic acid B. Carbonic acid C. Carboxylic acid D. None

Alcohols of low molecular weight are
A. Soluble in water B. Soluble in water on heating C. Insoluble in water D. Insoluble in all solvents

Methyl alcohol is not used
A. as a solvent B. as an anti freezing agent
C. as a substitute for petrol D. for denaturing of ethyl alcohol

When Phenol reacts with CH_3COCl the product formed is
A. Ether B. Alcohol C. Aldehyde **D. Ester**

Williamsons synthesis of ethers is superior to alcohols because it makes
A. Symmetrical ethers B. Asymmetrical ethers
C. Either at room temperature **D. Both symmetrical and asymmetrical ethers**

Diphenyl ether is also called
A. Phenoxy benzene B. Benzoxy benzene C. Hexoxybenzene D. Phenoxy ether

(v) Hydrogen bonding is maximum in
A. Ethanol B. Diethyl ether C. Ethyl chloride D. Triethyl amine

What is product in the following sequence of operations?
Chlorobenzene + NaOH ⟶ A + HNO_3 (conc.) ⟶ product
A. o-nitrophenol B. p-nitrophenol C. both a and 'b' **D. picric acid**

Which one of the following compounds does not contain carboxylic group
A. Acetic acid B. Formic acid **C. Picric acid** D. Benzoic acid

(xviii) In a reaction $C_2H_5\text{-}O\text{-}C_2H_5 + HI \rightarrow X$, then X should be
A. C_2H_5OH only B. C_2H_5I **C. C_2H_5OH and C_2H_5I** D. No reaction

SUBJECTIVE

Time: 2.35 Hours Total Marks Section B and C: 68

Section – B (Marks 42) (14 × 3 = 42)

2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

There are different structural isomers of formula C_4H_9OH
a. Draw the structures of the four Alcohols of formula C_4H_9OH 02
b. Classify these isomers as primary, secondary or tertiary 01

Ethanol is prepared on industrial scale world over
a. Name the process, temperature and enzymes used for the above process when ethanol is prepared from ... with equations. 02
b. Only 12% alcohol can be prepared by this process. Why? 01

[illegible]

[illegible]

a. [illegible] fermentation of molasses. Give reason. 1.5
b. [illegible] 1.5

a. Why [illegible] is a gas [illegible] a liquid? 01
b. Why does [illegible] in water? 01
c. Why does phenol show [illegible]? [illegible]

Ethers [illegible] functional group

a. Describe preparation of Ethers by Williamsons Synthesis 1.5
b. Why are Ethers slightly soluble in water? 1.5

a. What is difference between alcohols and phenols? 01
b. What are monohydric and polyhydric alcohols? 01
c. Write sturcutres of iso-butyl alcohol and sec-butyl alcohol. 01

(ix) How ethanol is prepared from starch? Write all balanced equations and conditions 03

(x) a. What is rectified sprit? 01
b. How rectified sprit may be converted into absolute alcohol? 02

(xi) a. Why lower alcohols are soluble in water? 1.5
b. Why melting and boiling points of alcohols are higher than corresponding alkanes? 1.5

(xii) Alcohols give variety of reactions
a. During reactions of alcohols under which conditions C-O bond breaks 1.5
b. Under which conditions O-H bond breaks during reactions of alcohols. 1.5

(xiii) a. Why tertiary alcohols are resistant towards oxidation? 01
b. Alcohols react with H_2SO_4 to give different products at different temperature. Give equations 02

(xiv) a. What is Lucas reagent? How will you differentiate between 1-propanol and 2-propanol by this reagent 02
b. What is Dow's process? 01

(xv) a. How will you differentiate between methanol and ethanol. 01
b. Write down the structural formulas of (i) Carbolic Acid (ii) Picric Acid 01
c. Give two uses of methyl alcohol 01

(xvi) a. Write IUPAC names of the following compounds A. $(CH_3)_2 CH OH$ B. $(CH_3)_2 CH CH_2 OH$ 02
b. How will you obtain phenol from benzenesulphonic acid? 01

(xvii) a. Alcohols and phenols both have OH group but phenols are more acidic than alcohols 02
b. Give one reaction of phenol in which it acts as an acid. 01

(xviii) a. Prepare benzene and picric acid from phenol? 01
b. How will you differentiate between an alcohol and phenol? 01
c. Water has higher b.p than alcohols. Why? 01

(xix) a. How will you obtain bakelite from phenol? 1.5
b. Ethyl alcohol is a liquid while methyl chloride is a gas. 1.5

Section - C

Note. Attempt any TWO questions All questions carry equal marks (2 × 13 = 26)

Q. 3. (a) What happens when 04
(i) Phenol is treated with acetyl chloride
(ii) Ethanol is reacted with ethyl magnesium bromide
(iii) Diethyl ether is reacted with PCl_5
(iv) Ethyl bromide is heated with silver oxide

(b) Give IUPAC names and structures of the following compounds. 05
(i) sec-butyl alcohol (ii) Lactic acid
(iii) ter-butyl alcohol (iv) Tartaric acid (v) Diphenyl ether

c. What is an Esterification reaction 02

d. What are simple and mixed ethers? 02

Q. 4. a. Show by reaction and diagram the industrial preparation of Methanol 03

b. How does phenol reacts with 04
(i) HNO_3 (ii) H_2SO_4 (iii) H_2/Ni (iv) NaOH

c. How does methanol reacts with 04
(i) $SOCl_2$ (ii) PCl_5 (iii) NH_3 (iv) CH_3COCl

d. Give four uses of phenol 02

Q. 9. a. Explain hydrogen bonding in alcohols, phenols and ethers? 03

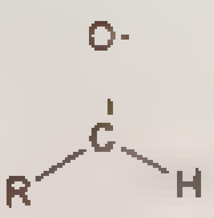
b. What is oxonium ion? How it can be generated from ethers? 03

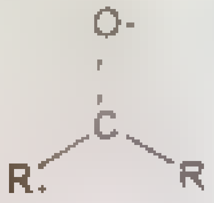
c. How may alcohols be oxidized? 03

d. Carry out the following conversions 04
(i) Benzene to cyclohexanol (ii) Ethanol to ethyl iodide

CHAPTER # 19

ALDEDHYDES AND KETONES





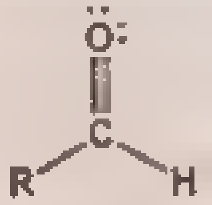
INTRODUCTION

Organic compounds containing the carbonyl functional group are called aldehydes and ketones.

ALDEHYDES

Functional Group. In aldehydes, the C-atom of carbonyl group is directly attached to at least [illegible]

Structure Formula: An aldehyde may be represented by the general formula structure

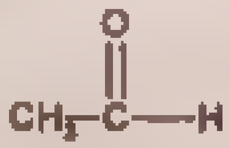


General Formula: The homologous series of aldehydes have general formula $C_nH_{2n}O$

Occurrence. Aldehyde groups are present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavors

Examples.

Formaldehyde

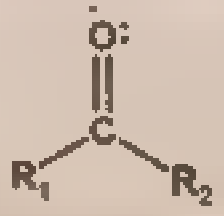


Acetaldehyde

KETONES

Functional Group: In ketones, the C-atom of carbonyl group is bonded to twp carbon atoms called ketonic group.

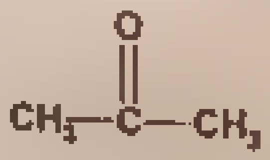
Structure Formula: A ketone may be represented by the general formula structure



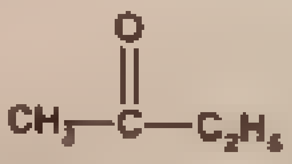
General Formula: The homologous series of ketones have general formula $C_nH_{2n}O$

Occurrence. Ketonic group is present in camphor and fructose

Examples:



Acetone



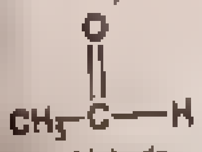
Methyl ethyl ketone

NOMENCLATURE:

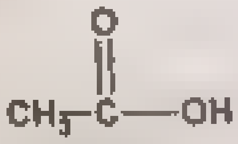
ALDEHYDES

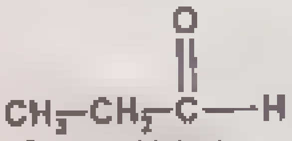
(a) COMMON NAMES:

- An aldehydes is named after the name of carboxylic acid obtained on its oxidation. the ending -ic acid is replaced by **aldehyde**

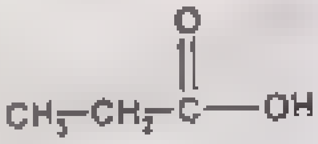

Acetaldehyde

from


Acetic acid


Propionaldehyde

from

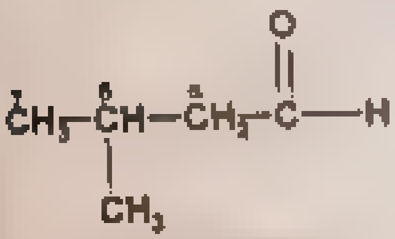

Propionic acid

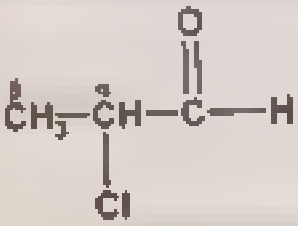

Butyraldehyde

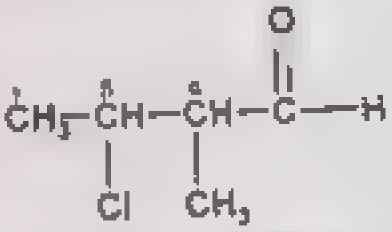
from


Butyric acid

- For naming substituted aldehyde the chain is labeled by using α, β, γ, etc. The carbon next to carbon of the carbonyl group is indicated by α and so on.


β-Methylbutyraldehyde


α-Chloropropionaldehyde

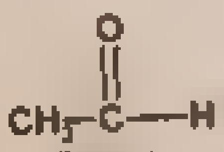

β-Chloro-α-methylbutyraldehyde

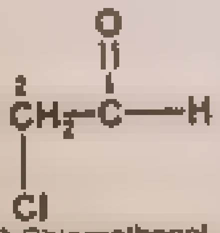
(b) IUPAC NAMES.

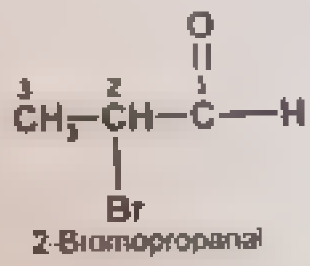
1. The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon
2. The ending e of the alkane is replaced by al
3. The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number 1
4. The position of the substituent is indicated by numbers which is written before their number

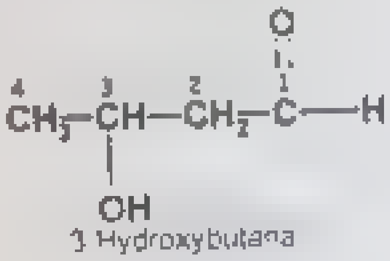
Examples:

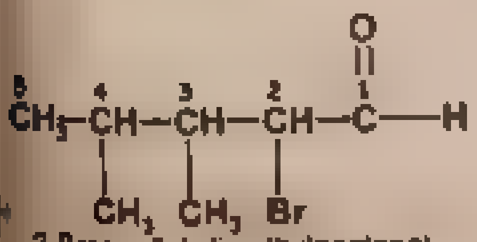

Methanal

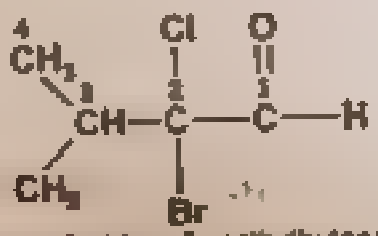

Ethanal

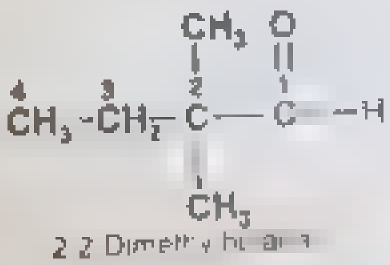

2-Chloroethanal

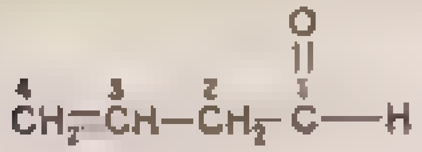

2-Bromopropanal

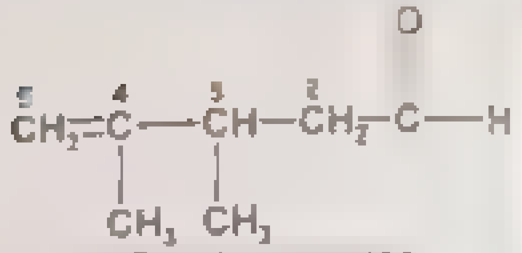

3-Hydroxybutanal


2-Bromo-3,4-dimethylpentanal


2-Bromo-2-chloro-3-methylbutanal


2,2-Dimethylbutanal

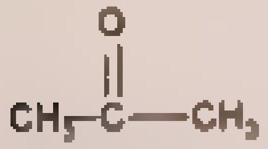

3-Butenal

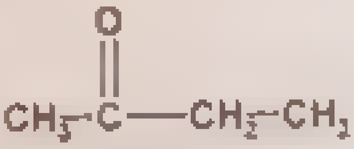


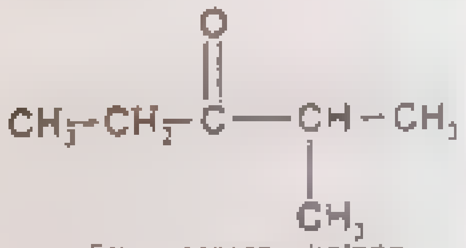
KETONES

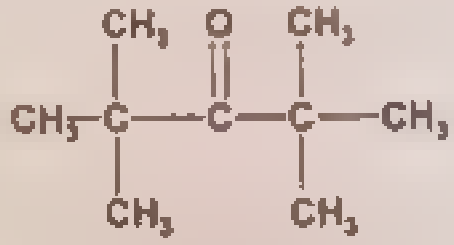
(a) COMMON NAMES.

- Ketones are names by adding the word ketone after ... carbonyl carbon in alphabetical order.

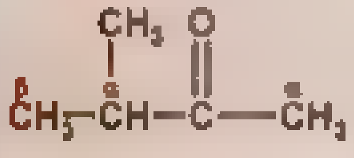

Dimethyl ketone


Ethyl methyl ketone

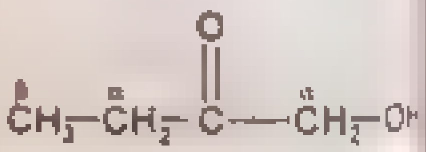

Ethyl isopropyl ketone


Ditertiarybutyl ketone

- Substituted ketones are named by labeling the chain using α, β ... etc. The carbon next to the carbonyl group is indicated by 'α' and so on, e.g.

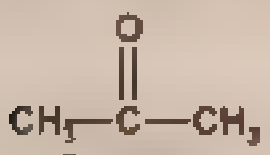

Methyl α-methylethyl ketone


Methyl β-chloroethyl ketone

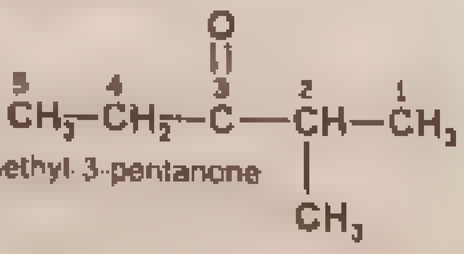

α hydroxymethyl ethyl ketone

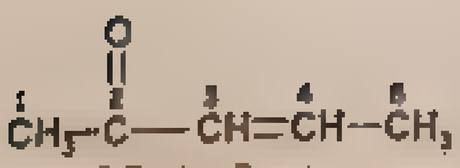
(b) IUPAC NAMES.

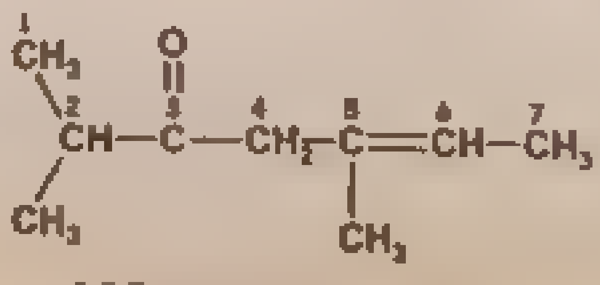
1. The longest chain containing the carbonyl group is taken a parent hydrocarbon
2. The ending e of hydrocarbon is replaces by one
3. The numbering starts from the end that gives the carbonyl carbon the lower number. In cyclic ketones carbonyl carbon is number 1
4. The positions of substituent are indicated by numbers before their names.

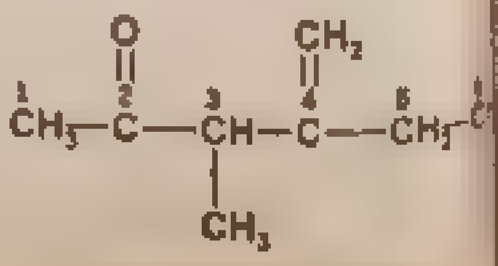

Propanone

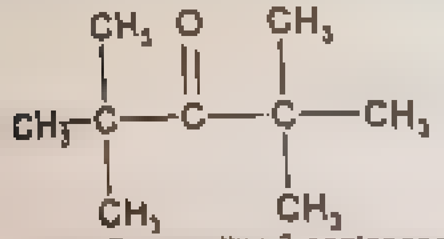

2-Butanone


2-Methyl-3-pentanone

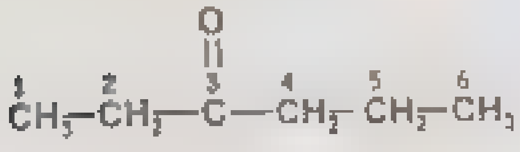

3-Penten-2-one


2,5-Dimethyl-5-hepten-3-one


3-Methyl-2,4-hexanedione


2,2,4,4-Tetramethyl-3-pentanone

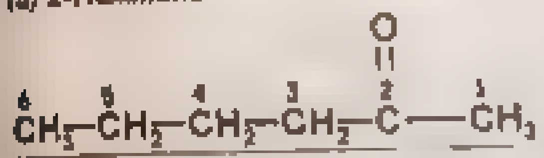

2-Pentanone


3-Hexanone

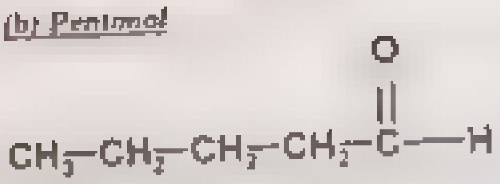
QUICK QUIZ-1

(i) Write the structures of the following compounds

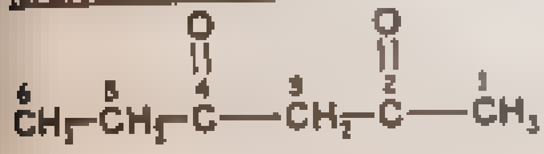
(a) 2-Hexanone



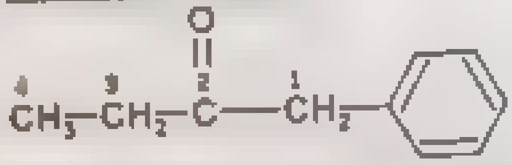
(b) Pentanal



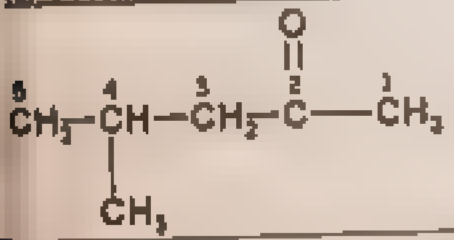
(c) 2,4-Hexanedione



(d) 1 Phenyl-2-butanone



(e) 4-Methyl-2-pentanone

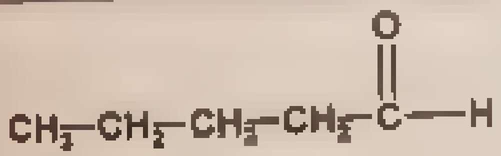


(f) 1 Phenyl-3 (2 methoxy phenyl)-1,3 propanedione

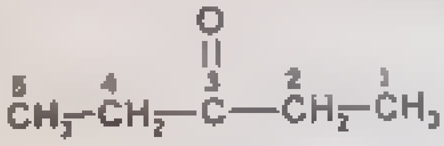
Incorrect Name. There is no propanedione

(ii) Give the IUPAC names of the followings

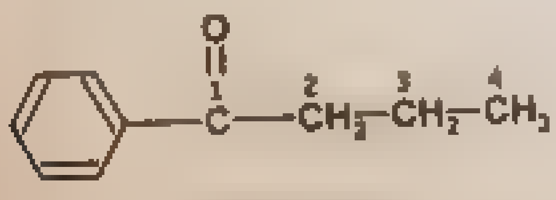
(a)


Pentanal

(b)

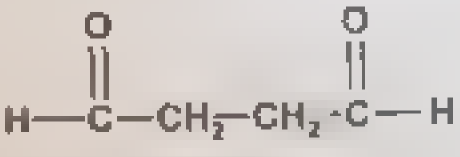

3-Pentanone

(c)

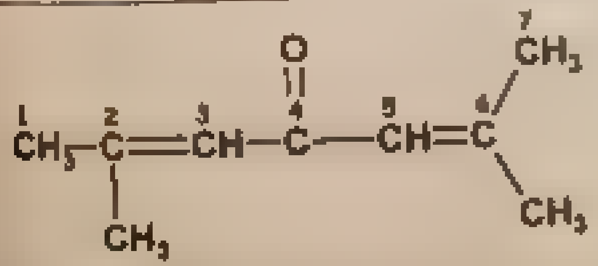

1-Pheny -1-butanone

(d) $OHC-CH_2-CH_2-CHO$

Or


Butanedial

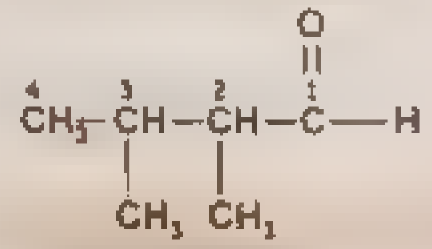
(e)


2,6-Dimethylhepta-2,5-dien-4-one

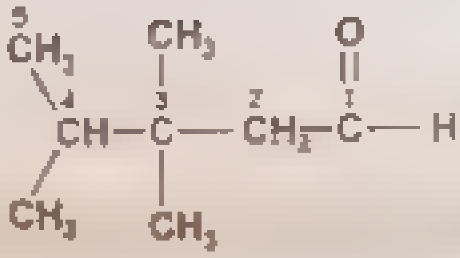
MORE PRACTICE

ALDEHYDES

$CH_3CH(CH\ )CH(CH\ )CHO$

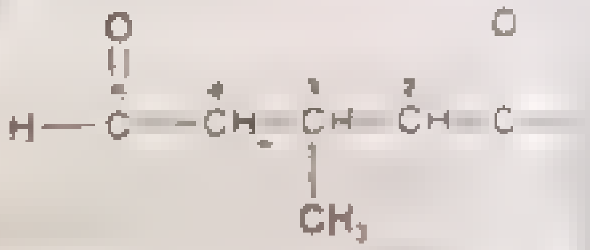


2 3-Dimethy bu anal

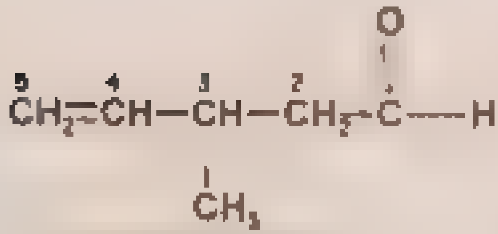


3 3 4-Trimethylpentanal

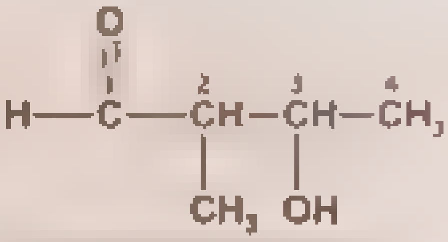
OHC CH CH CH CH CH



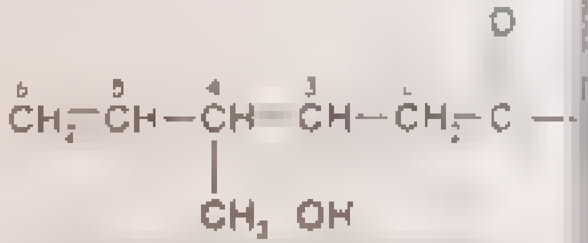
3-Methy penta



3-Methyl-4-pentenal

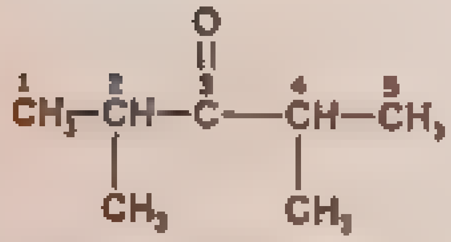


3-Hydroxy 2 methylbutanal

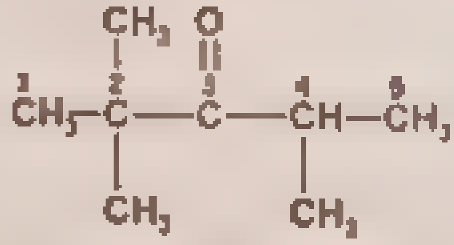


[illegible]

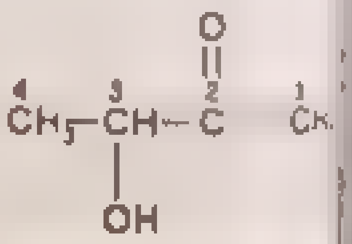
KETONES



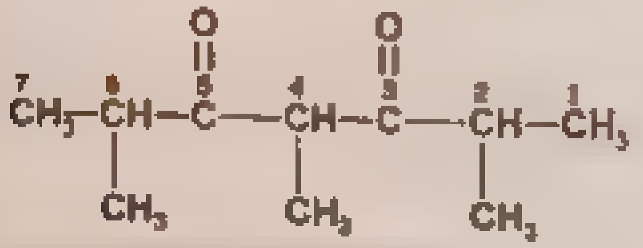
2 4-Dimethyl-3-pentanone



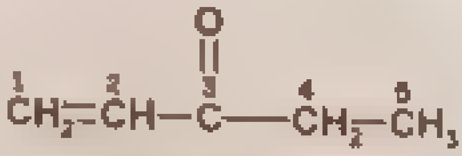
2 2 4 Trimethyl-3-pentanone



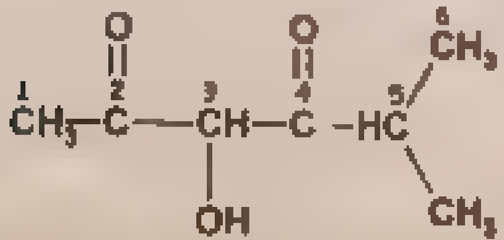
3 Hydroxy 2 butanone



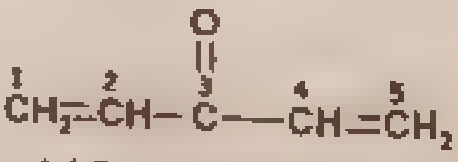
2 4 6-Trimethyl-3 5-heptanedione



1-Penten-3-one



3-Hydroxy-5-methyl-2,4-hexanedione



1,4-Pentadien-3-one

PHYSICAL PROPERTIES

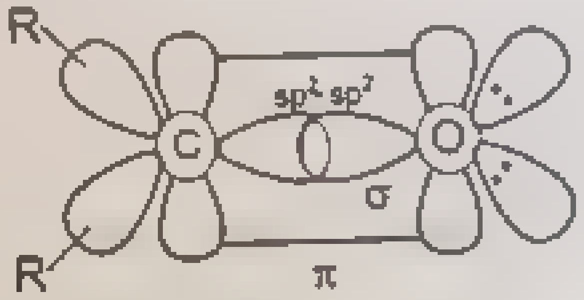
- The C = O bond has polar nature due to the electronegativity difference of the atoms
- The polar nature of the C = O means that dipole-dipole interactions will occur
- The C=O bonds cannot form hydrogen bond with each other. However the C=O can accept hydrogen bonds from hydrogen bond donors (e.g. water, alcohols)

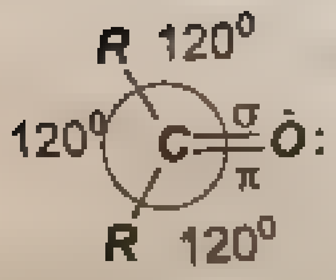
The results of these effects are

- higher melting and boiling points compared to analogous alkanes
- lower boiling points than analogous alcohols
- more soluble than alkanes but less soluble than alcohols in aqueous media

STRUCTURE

- The carbonyl group consists of an O atom bonded to a C atom via a double bond
- In carbonyl group both carbon and oxygen are sp^2 hybridized
- A sigma bond is formed between C and O by the overlap of sp^2 hybrid orbitals of C & O
- Two lone pairs of oxygen are present in two sp^2 hybrid orbitals while carbon uses its two sp^2 hybrid orbitals to form bond with other groups like alkyl groups R
- Both C and O contain one unhybridized p – orbital each which overlap sideways to form a pi-bond
- Three groups attached to the carbonyl carbon lie in same plane with bond angles of approximately 120°

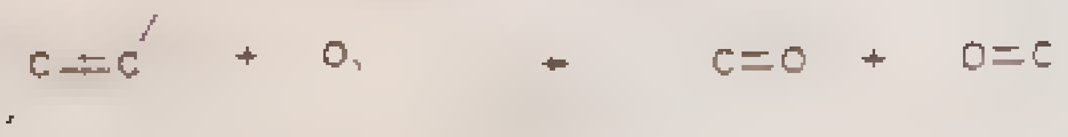




- Electron density between C and O is not equally shared.
- Oxygen due to its greater electronegativity, attracts charged cloud more towards itself. As a result O acquires δ⁻ charge and C acquires δ⁺ charge. Thus carbonyl group becomes polar.

PREPARATIONS OF ALDEHYDES AND KETONES

(1) OZONOLYSIS OF ALKENES



Reaction type **Electrophilic Addition**

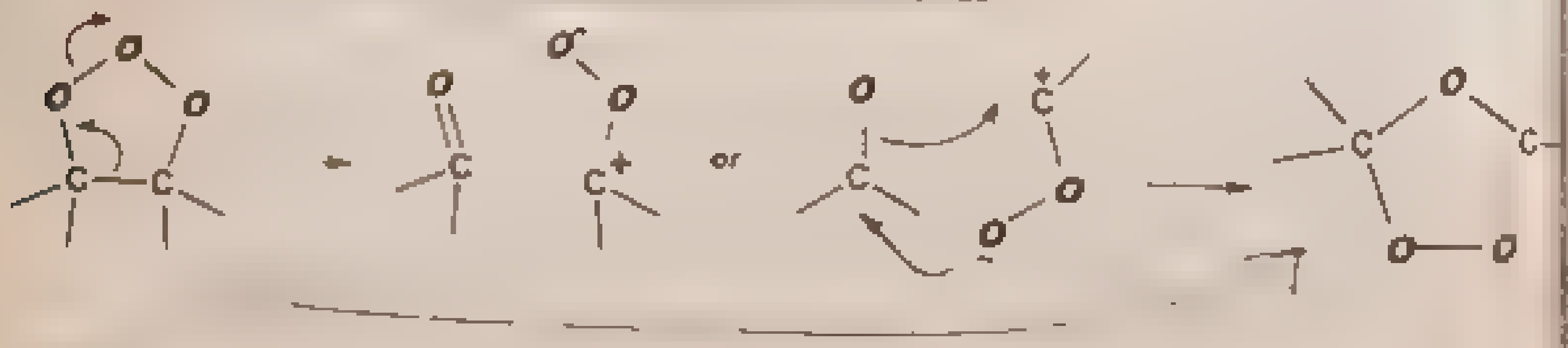
- ***Overall transformation.*** C=C to two C=O
- ***Reagents***

MECHANISM

Step 1

Step 2

The cyclic species called the mol...

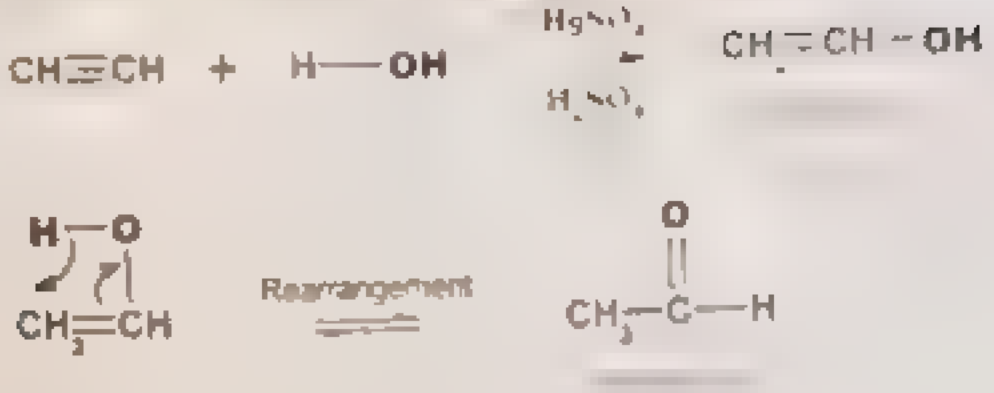


Step 3

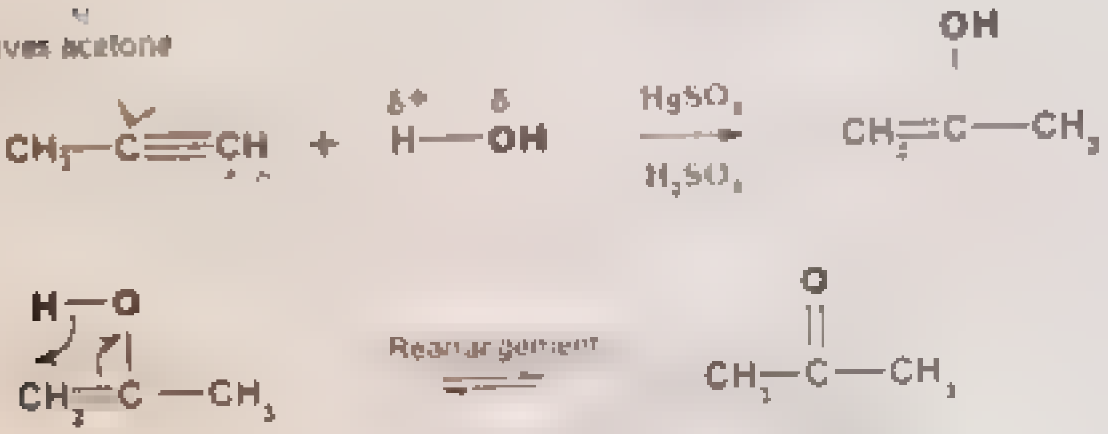
On work-up (usually Zn / acetic acid) the malozonide decomposes to give two carbonyl compounds

(2) HYDRATION OF ALKYNES

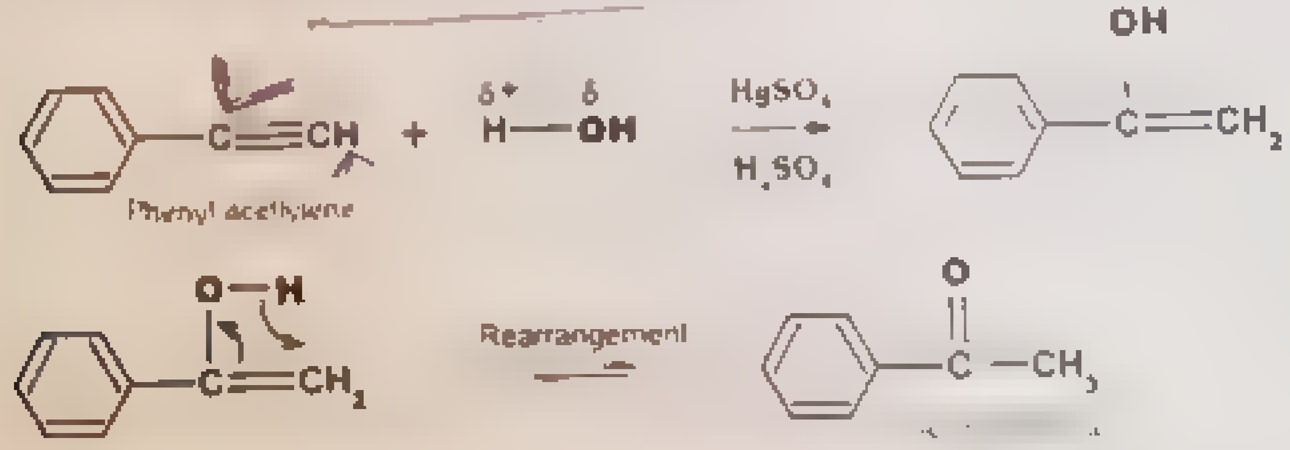
- Water adds [illegible]
- Enol forms as intermediate which isomerizes



- Propyne gives acetone



- This reaction is useful for preparing methyl aryl ketones



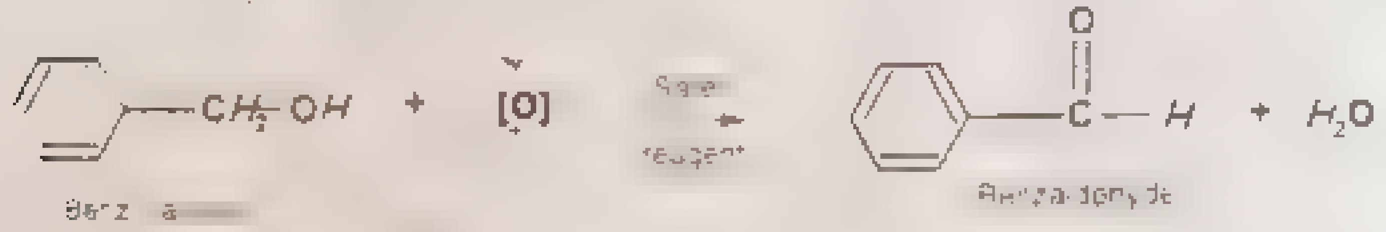
(3) OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS

- Primary alcohols are oxidized to aldehydes by
  (i) warming with acidic dichromate solution or
  (ii) Jone reagent (CrO_3 + dil. H_2SO_4 + acetone) or
  (iii) Sarett reagent (CrO_3 in pyridine)

(i) $\underset{\text{Ethanol}}{CH_3-CH_2-OH} + [O] \xrightarrow[\text{conc } H_2SO_4]{Na_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + H_2O$

$$CH_3-CH_2-CH_2-CH_2-OH + [O] \longrightarrow CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2O$$

Butanal

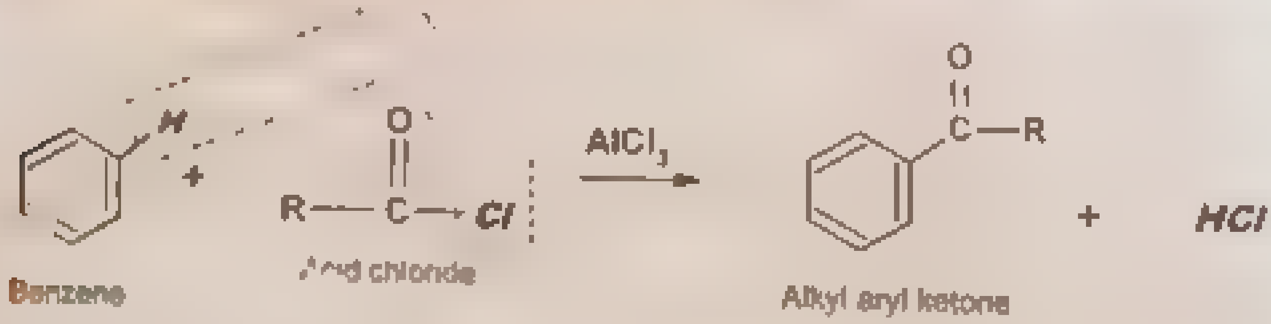


- [illegible]
- Secondary alcohols are oxidized to ketones.

$$CH_3-\underset{CH_3}{\underset{|}{CH}}-OH + [O] \xrightarrow[\text{conc. } H_2SO_4]{Na_2Cr_2O_7} CH_3-\underset{CH_3}{\underset{|}{C}}=O + H_2O$$

(4) FRIEDEL-CRAFTS ACYLATION OF BENZENE

- [illegible] AlCl₃ [illegible]

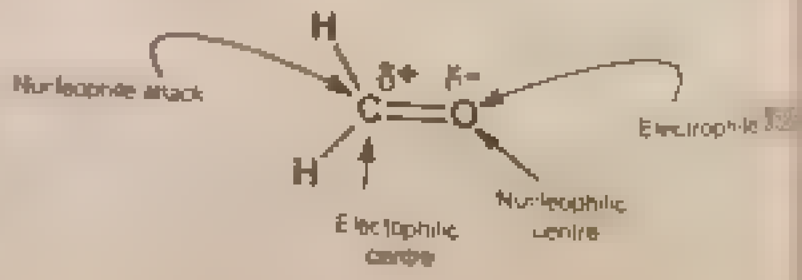


- $AlCl_3$ generates an acylium ion $R-\overset{O}{\overset{\|}{C^+}}$ electrophile which is substituted in the aromatic ring.

Exercise Q3 (i) What is the reactivity of the carbonyl group?

REACTIVITY

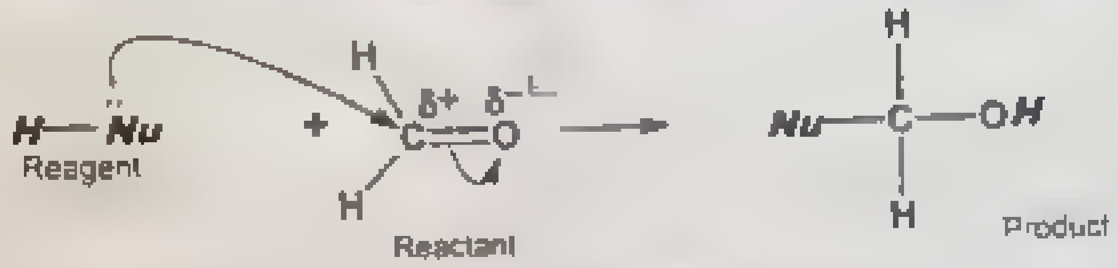
- The double bond of the carbonyl group has a σ bond and a π bond.
- As oxygen is more electronegative, it attracts the π-electrons to itself. This attraction makes the carbonyl group a polar group.
- The oxygen atom has a partial negative charge on it and the carbon atom has partial positive charge.
- Hence, it makes oxygen atom nucleophile and carbon atom becomes electrophile.



REACTIONS OF ALDEHYDES AND KETONES

NUCLEOPHILIC ADDITION

The general reaction of nucleophilic addition is given below.



There are two types of nucleophilic addition reactions of carbonyl compounds

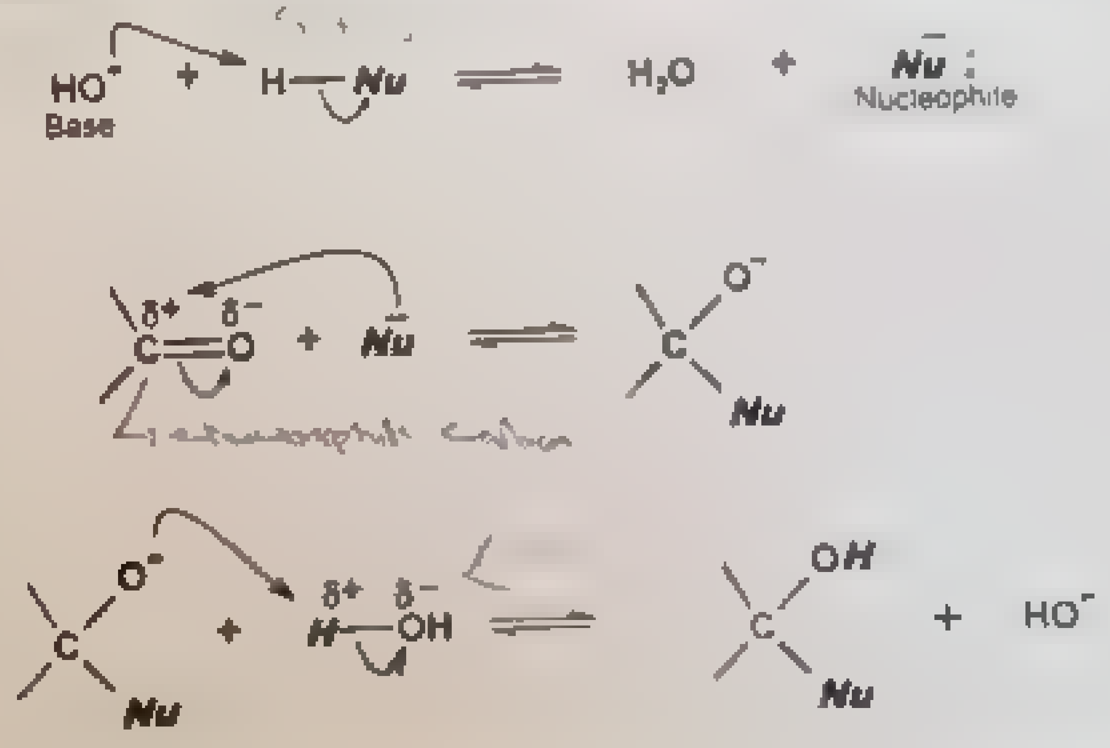
(i) Base catalysed nucleophilic addition reaction

(ii) Acid catalysed nucleophilic addition reaction

(i) BASE CATALYSED

- A base catalysed nucleophilic addition reaction takes place with a strong nucleophilic reagent
- The base reacts with the reagent ad generates the nucleophile
- The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group

GENERAL MECHANISM



There are five types of base catalysed nucleophilic addition reactions of carbonyl compounds

(1) Addition of hydrogen cyanide

(2) Addition of Grignard's reagent

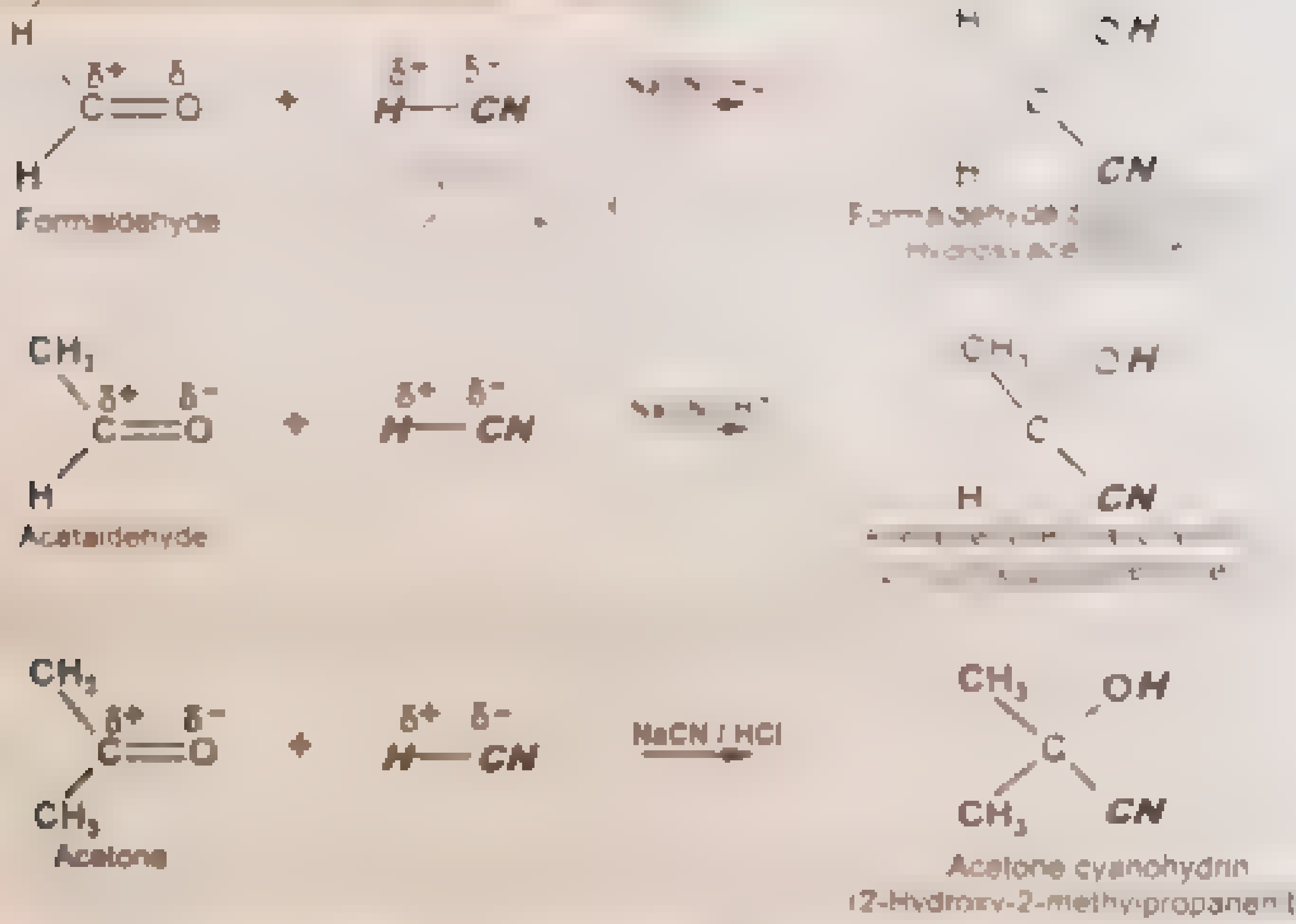
(3) Addition of sodium bisulphate

(4) Condensation reactions

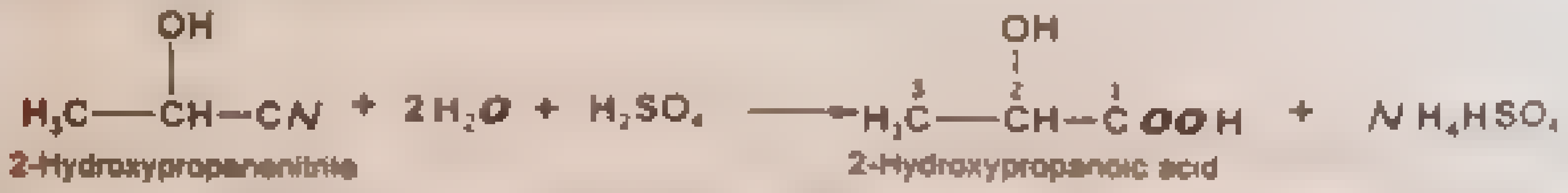
(5) Holoform reactions

ADDITION OF HYDROGEN CYANIDE

- Hydrogen cyanide adds to aldehydes & ketones [illegible]
- The acid generates [illegible]



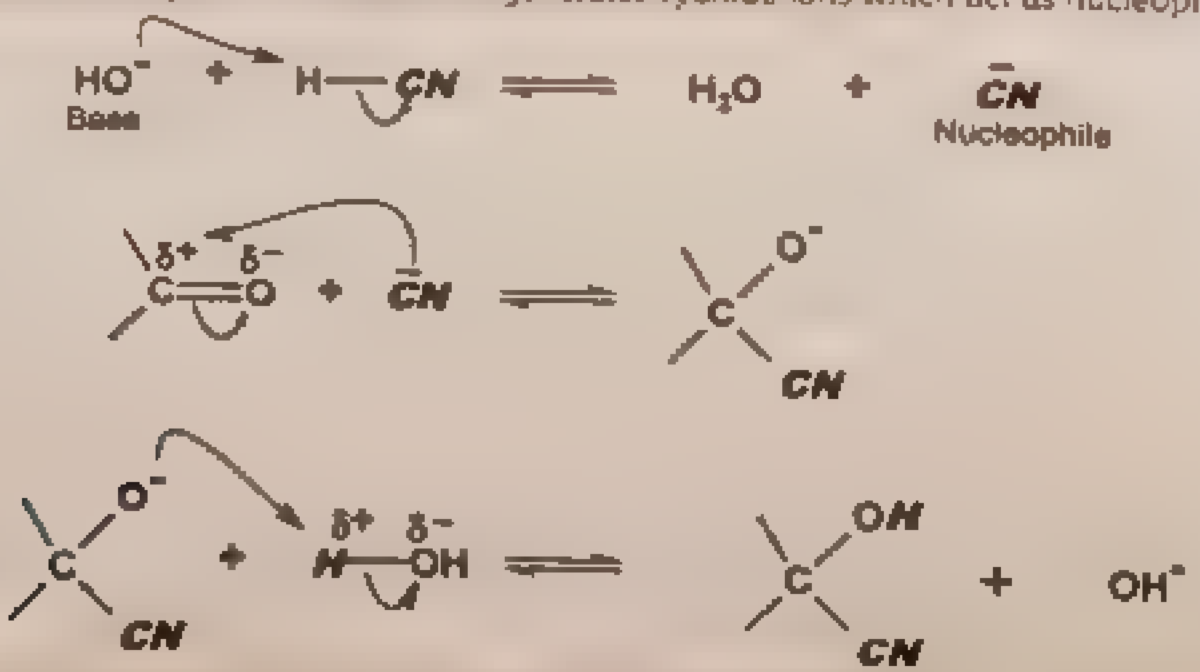
- The reaction is used in the synthesis of α hydroxy acid. These acids contain [illegible] carbon atom more than number of carbon atoms in the starting aldehydes or ketones.



Exercise Q2 (iii) What is the mechanism of HCN addition to carbonyl compounds?

Mechanism

The reaction is base catalysed. The base OH^- generates cyanide ions which act as nucleophile.

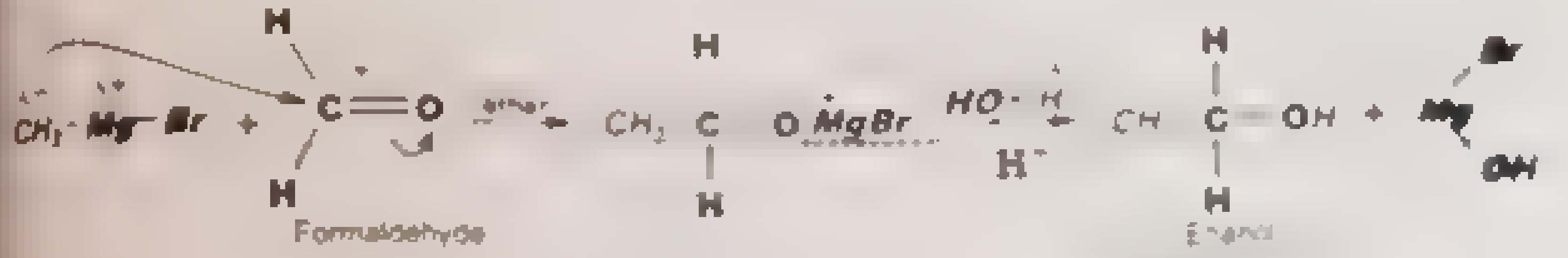


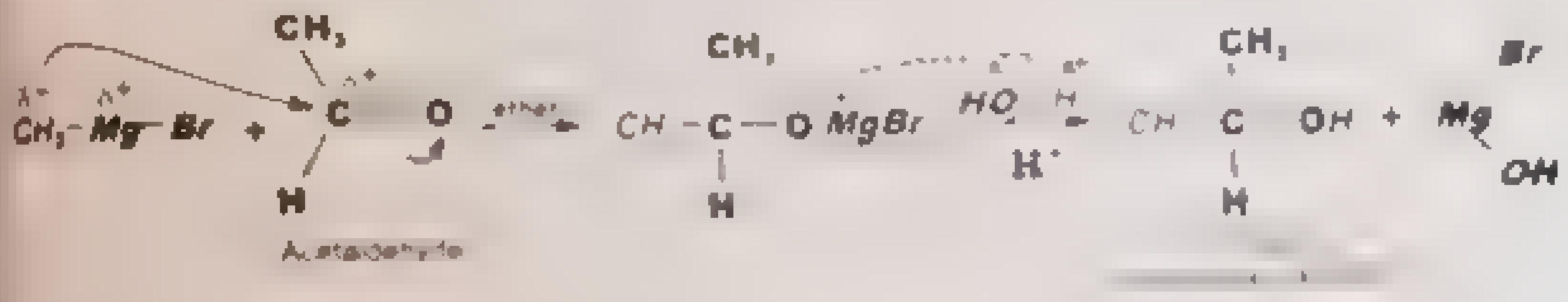
The hydroxide ion liberated reacts with undissociated hydrogen cyanide. Thus, it produces more cyanide ions, which in turn react with more carbonyl compound.

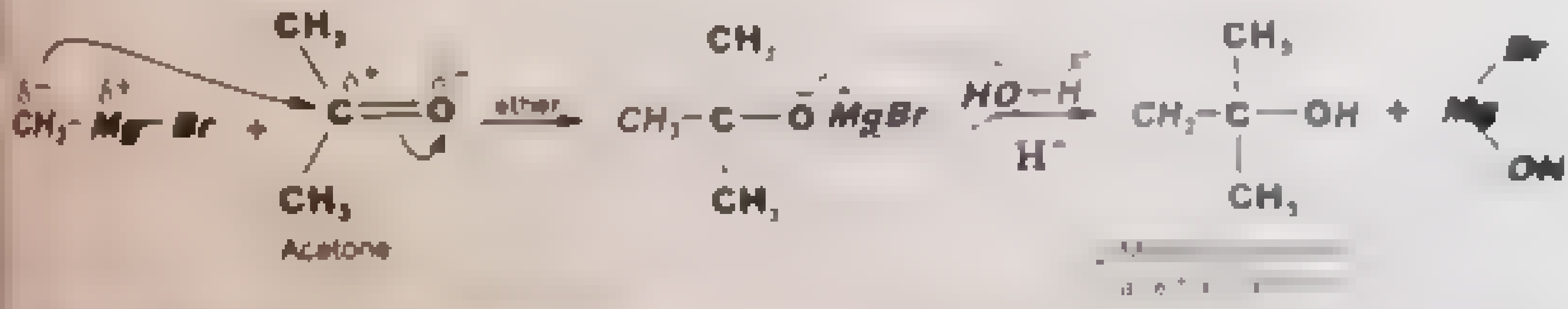
Exercise Q7 : What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?

(2) ADDITION OF GRIGNARD'S REAGENT

Grignard's reagent ... add ... with a dilute mineral acid give alcohols

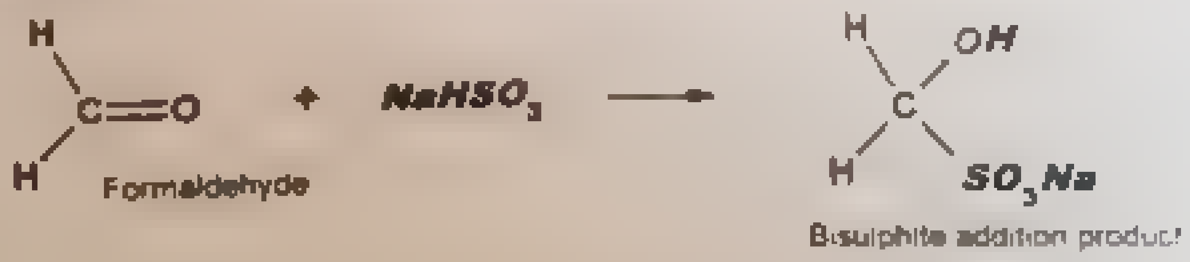


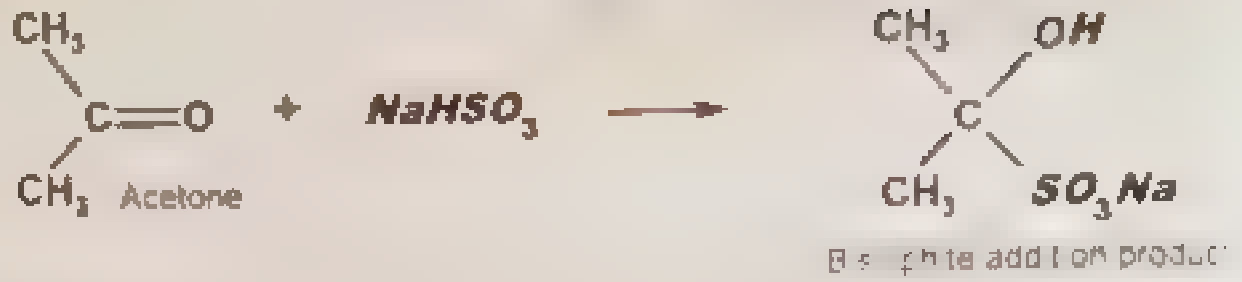




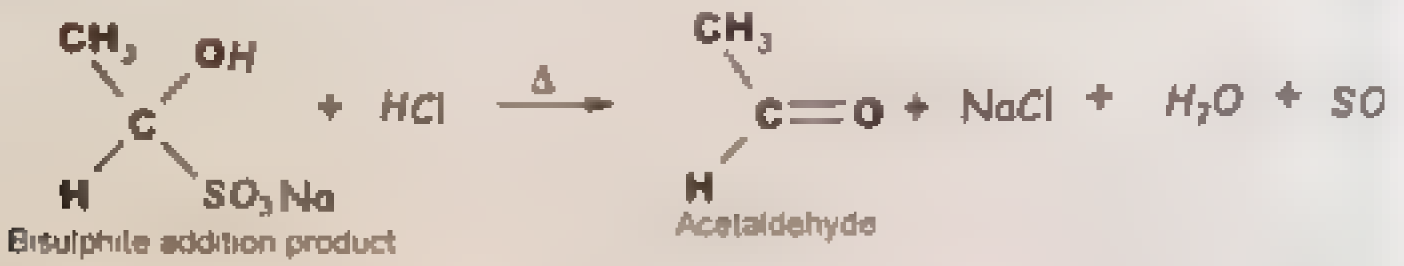
(3) ADDITION OF SODIUM BISULPHATE

- Aldehydes and small methyl ketones react with a saturated aqueous ... crystalline white precipitate of sodium bisulphate adduct





- Bisulphite on heating a dilute mineral acid HCl or H_2SO_4 ...



- The reaction is used for the separation and purification of carbonyl compounds from non compounds such as alcohols

Exercise Q2 (x) Give the mechanism of addition of sodium bisulphate to ketones

Mechanism

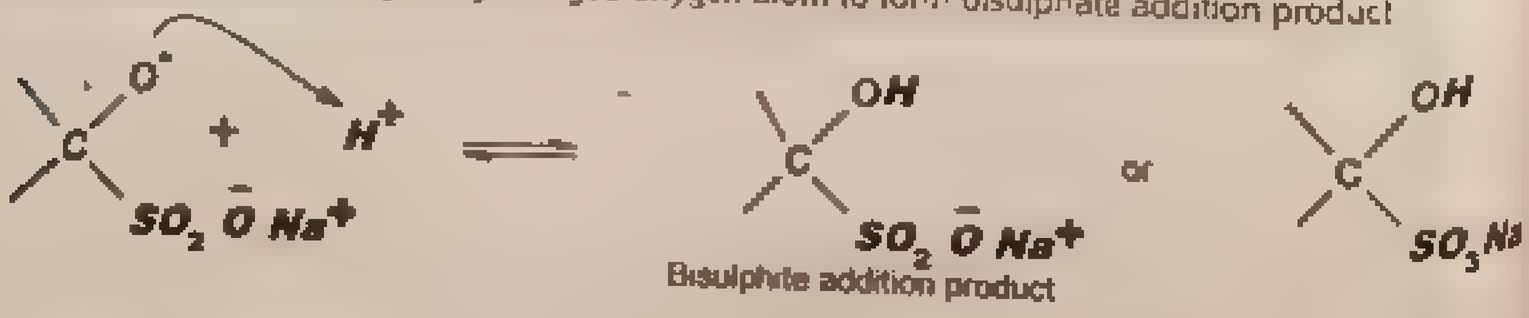
- Sodium bisulphate ionizes to form sulphate ions

$$NaHSO_3 \rightleftharpoons \bar{S}O_2-O^- + Na^+ + H^+$$

Nucleophile

- The sulphite ion acts as a nucleophile since the sulphur atom is more nucleophilic than oxygen ... formed

- Proton is attached to the negatively charged oxygen atom to form bisulphate addition product



- Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite

(1) CONDENSATION REACTIONS

The reaction in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like H_2O or NH_3 are called condensation reactions

Exercise Q3 (iv) *Define and explain aldol condensation along with mechanism.*

(a) ALDOL CONDENSATION

Aldol condensation is a reaction in which two molecules of same or different carbonyl compound containing α-hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to from aldol or ketol, which usually loses water molecule

Mild Alkaline conditions.

Aldol condensation takes place un[illegible] presence of sodium carbonate sodium bicarbonate, barium hydroxide [illegible]

Types:

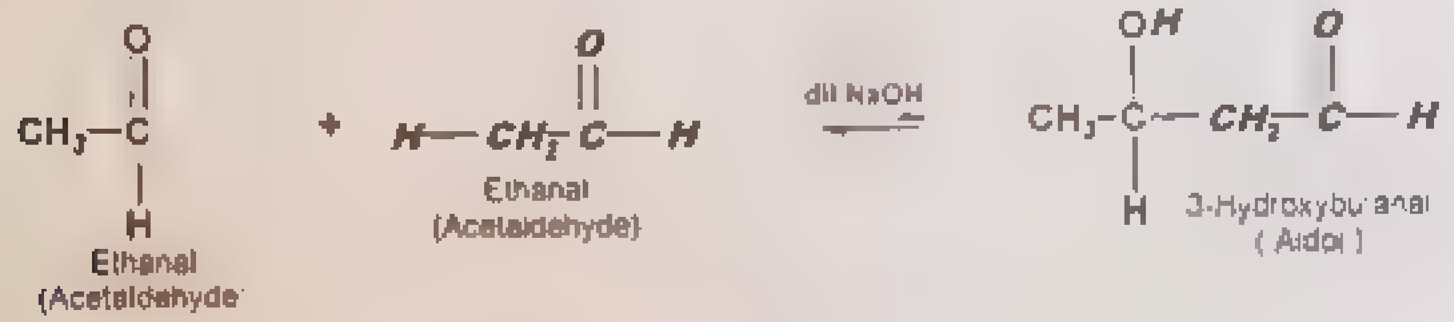
Aldol condensation can occur

(i) Between two aldehydes (identical or different)

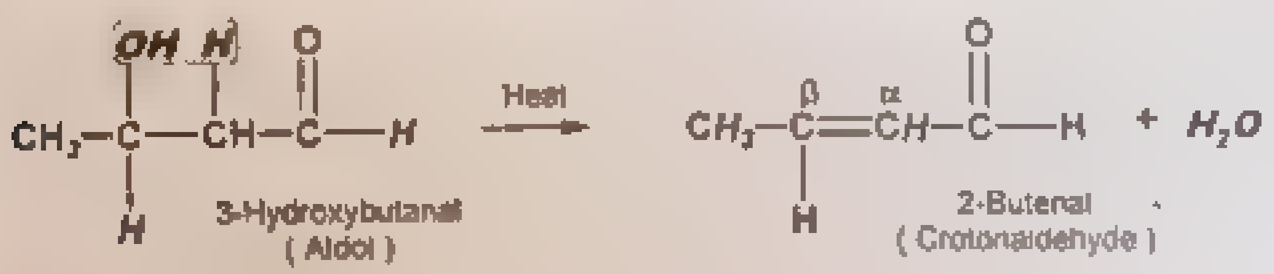
(ii) Between an aldehyde and a ketone

(iii) Between two ketone (identical or different

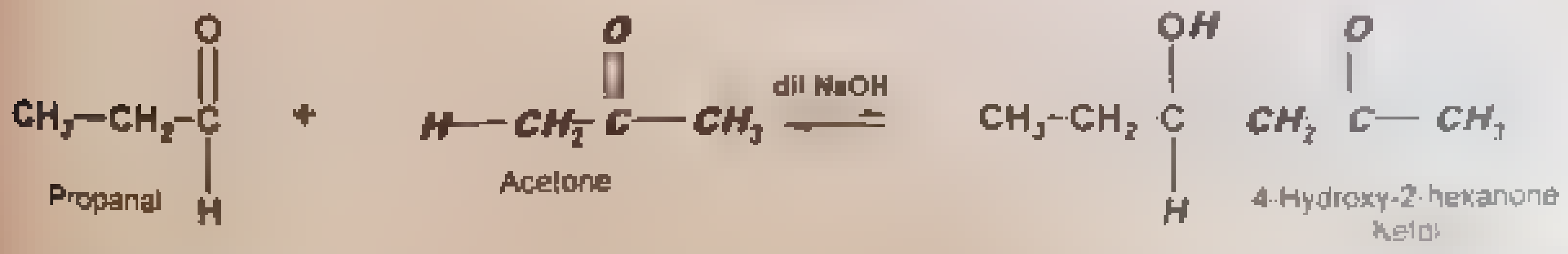
(i) Condensation between two aldehydes.



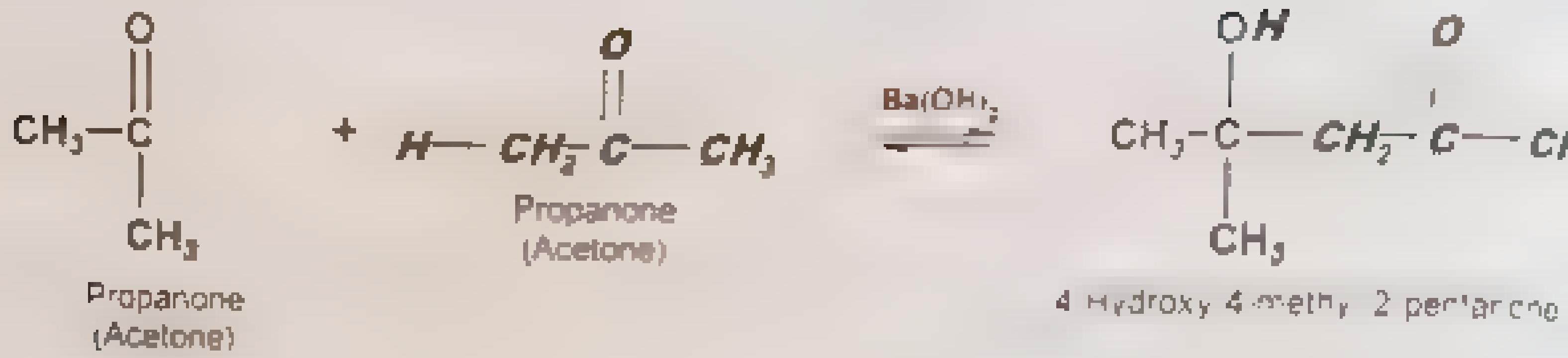
On heating aldol loses a molecule of water to form α, β-unsaturated aldehyde



(ii) Condensation between aldehyde and ketone:



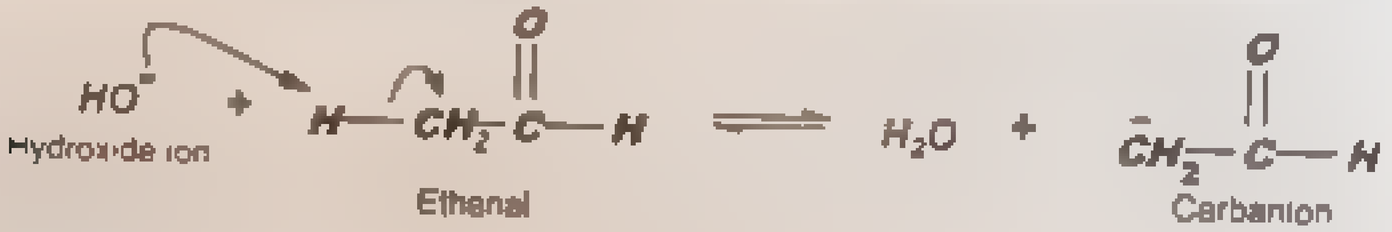
(iii) Between two ketones



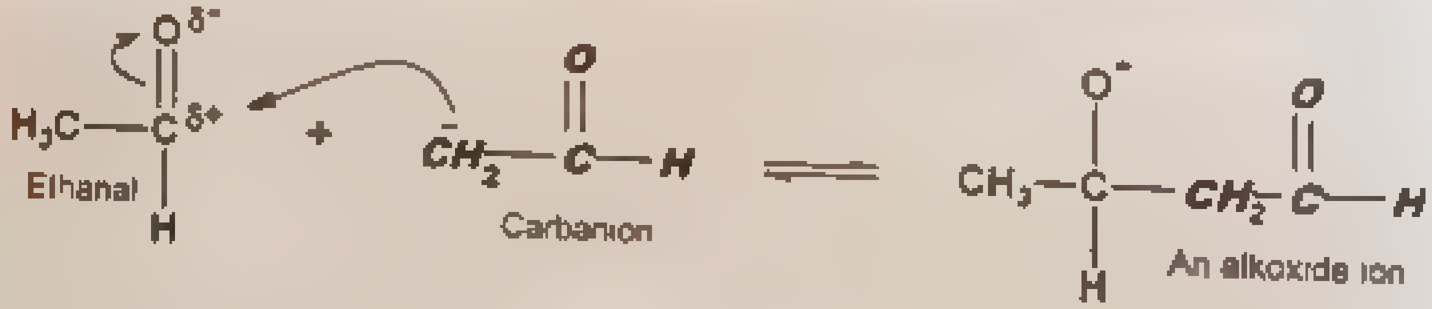
Mechanism of Aldol Condensation:

Following steps are involved in aldol condensation

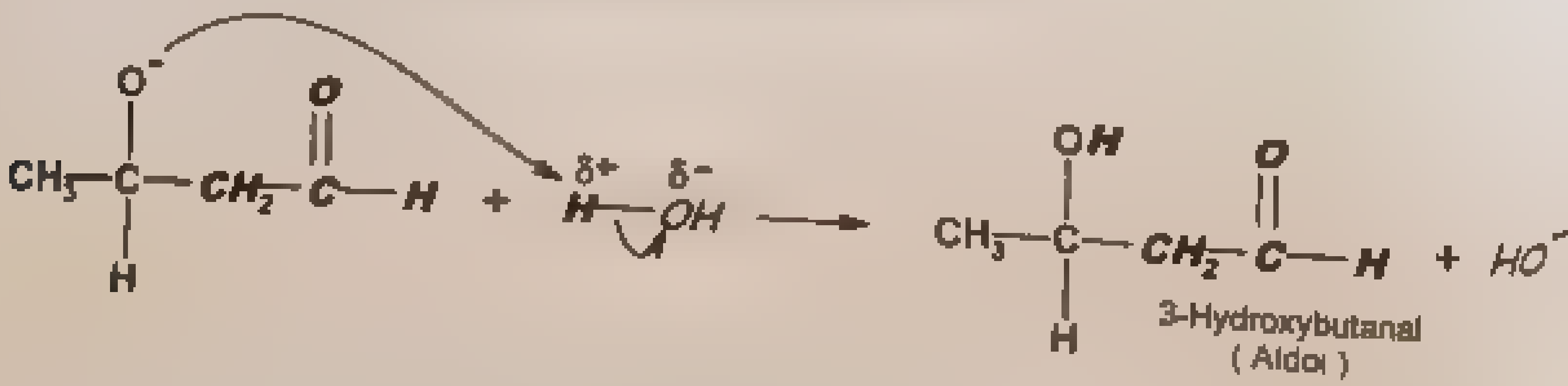
(1) Removal of a proton from α-carbon of aldehyde/ketone by base. (Formation of nucleophile)



(2) Attack of nucleophile on carbonyl carbon to form alkoxide ion. (Formation of alkoxide ion)



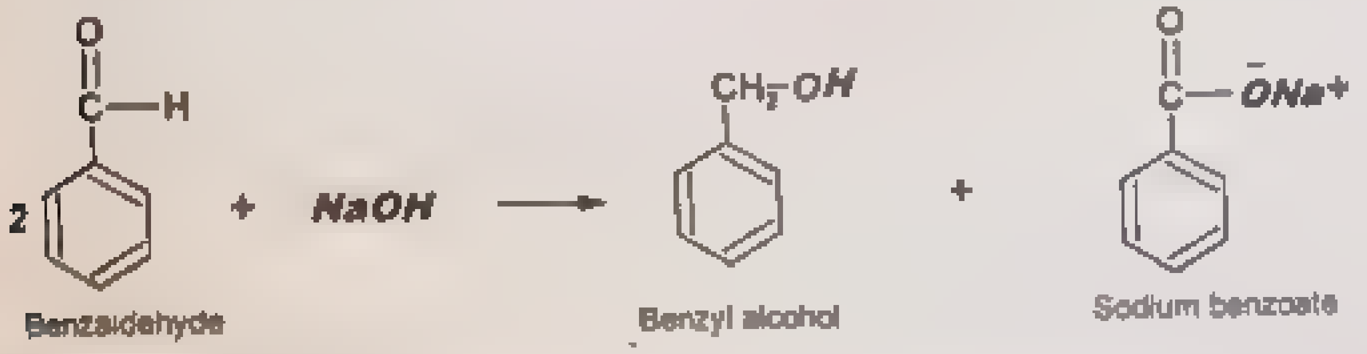
(3) Removal of proton from water by alkoxide ion. (Formation of aldol)



Exercise Q3 (viii) Which type of aldehydes give Cannizzaro's reaction? Explain with mechanism

(b) CANNIZZARO'S REACTION

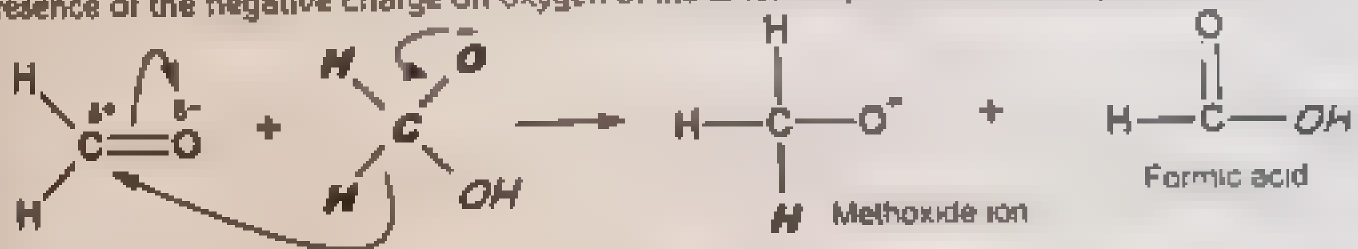
- Aldehydes having no α-hydrogen atoms undergo Cannizzaro's reaction
- It is a disproportionate (self oxidation-reduction) reaction
- Two molecules of the aldehyde are involved.
- One molecule is reduced into corresponding alcohol and the other is oxidized into the acid or the salt form
- The reaction carried out with 50% aqueous solution of sodium hydroxide at room temperature



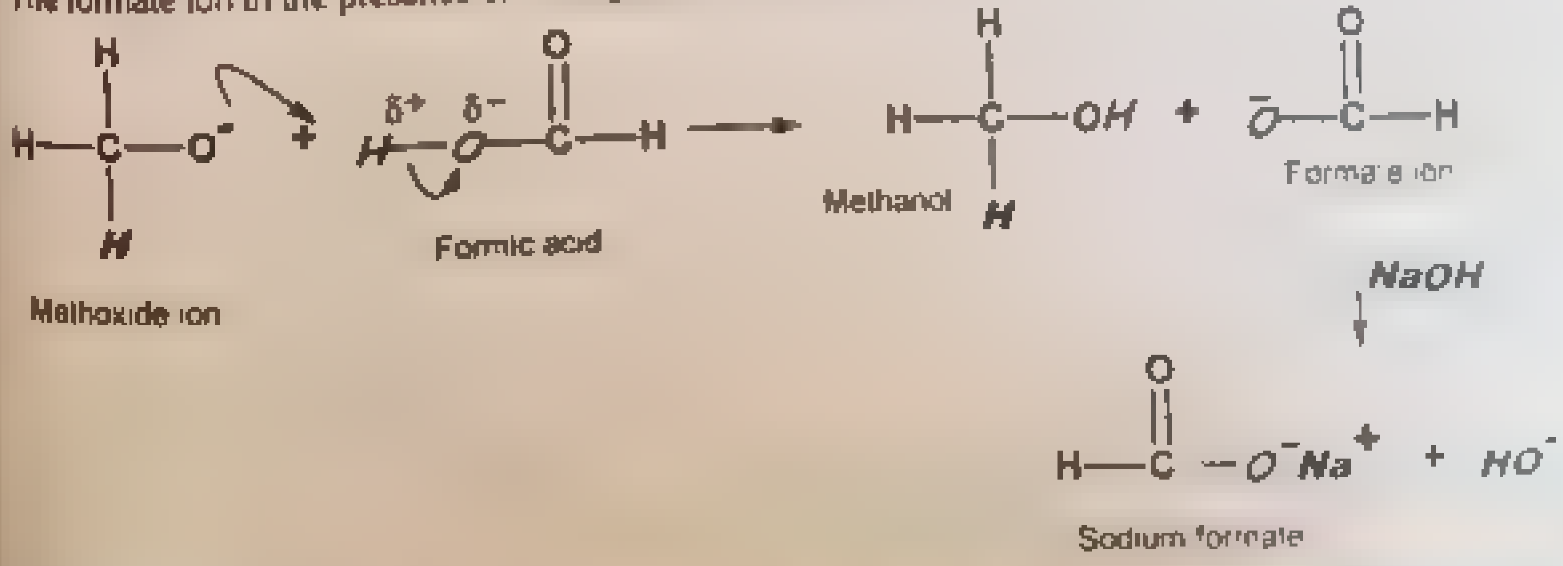
Mechanism of Cannizzaro's Reaction:

- The hydroxide ion acts as a nucleophile. It attaches on the electrophilic carbonyl carbon to form a complex anion.

- The anion transfers a hydride ion to second molecule of formaldehyde
- The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion



- The methoxide ion acts as a base and abstracts a proton from formic acid to form methanol and formate ion
- The formate ion in the presence of alkali gives a salt of acid



Exercise Q3 (e) Give detail of haloform reaction. Why it is called so

(5) HALOFORM REACTION

- Only acetaldehyde and

- Secondary alcohols containing the methyl group also undergo this alcohol that gives this reaction

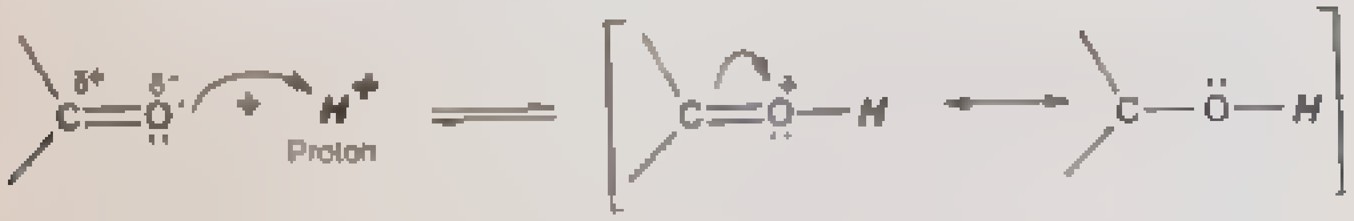
- Halogen reaction is a convenient method for converting a methyl ketone to a carboxylic acid contain carbon atom less than parent compound

IODOFORM TEST

- It is haloform reaction in which iodine and aqueous sodium hydroxide form water insoluble (a yellow solid)
- Iodoform test is used for distinguishing methyl ketones from other ketones
- It is also used to distinguish ethanol form methanol and other primary alcohols
- It can be used to distinguish acetaldehyde from other aldehydes

(II) ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

- The addition is initiated ... the p...
- It increases the electrophilic character ... electrophilic carbon becomes ...



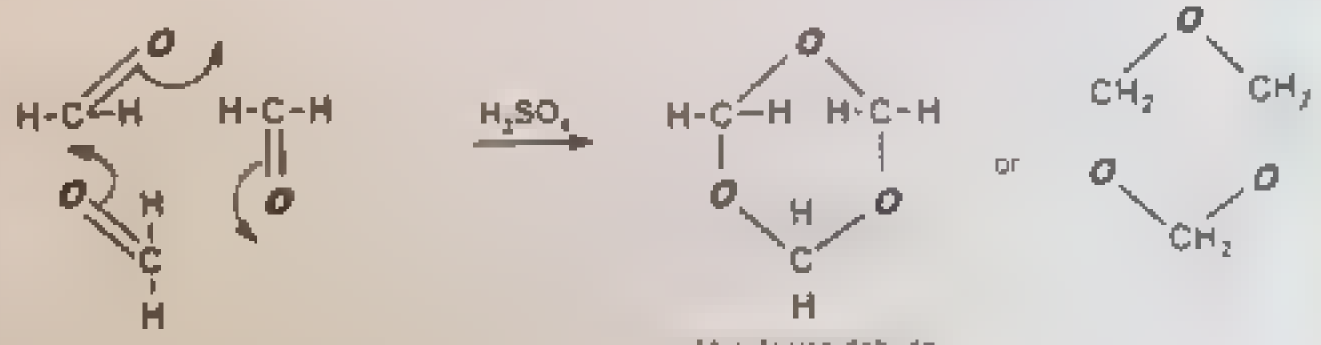
There are three types
(1) Polymerization
(2) Addition of ammonia derivatives
(3) Addition of alcohols

(1) POLYMERIZATION

Both formaldehyde and acetaldehyde polymerize in the presence of ... and paraldehyde

3 HCHO or

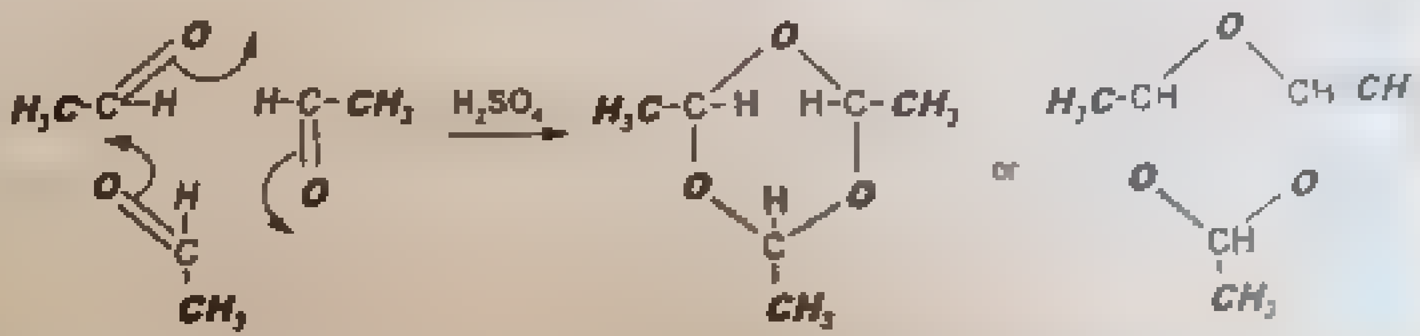
Formaldehyde



Metaformaldehyde

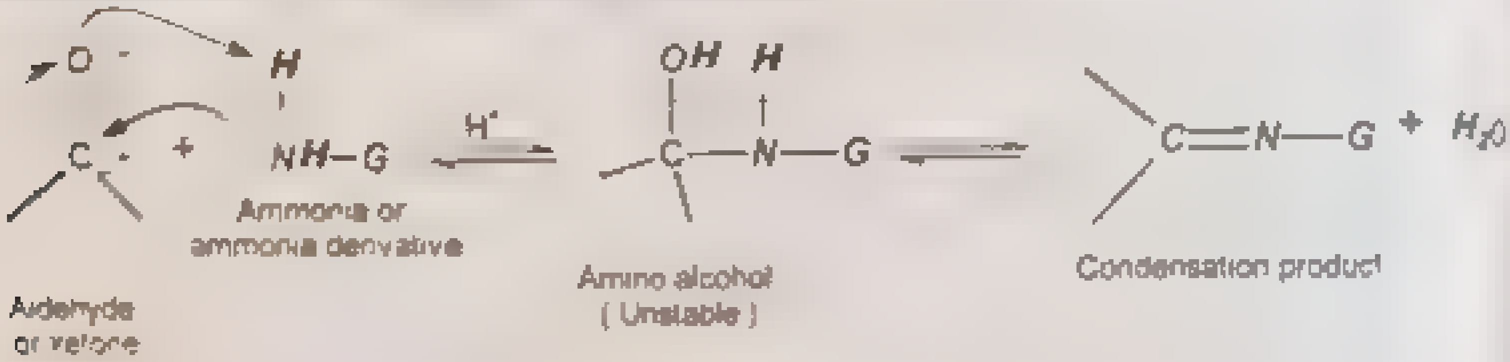
3 CH_3CHO or

Acetaldehyde



Paraldehyde

(2) ADDITION OF AMMONIA DERIVATIVES

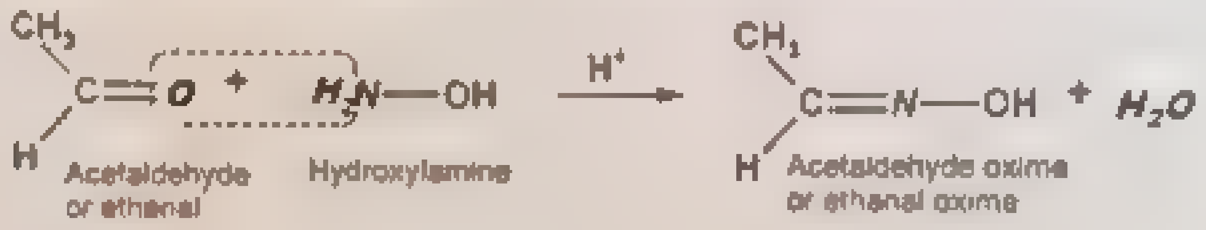


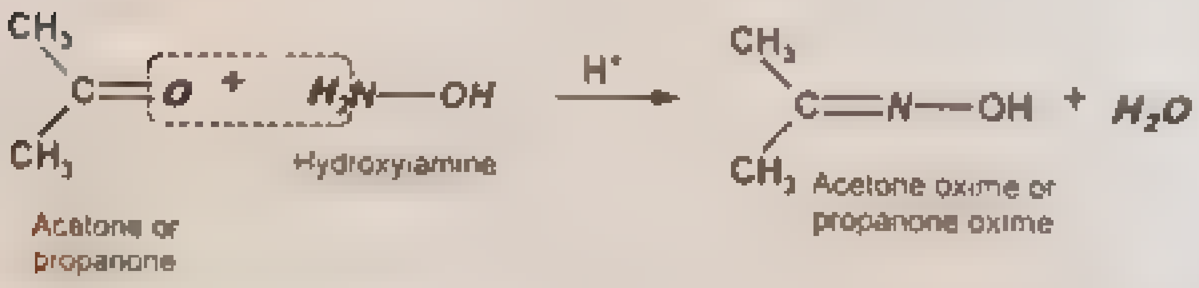
Specific Examples

Some commonly used ammonia derivatives are hydroxylamine NH_2OH, hydrazine NH_2NH_2, phenylhydrazine $C_6H_5NHNH_2$, semicarbazide $NH_2NHCONH_2$ and 2,4-dinitrophenylhydrazine $NH_2NHC_6H_3(NO_2)_2$

REACTION WITH HYDROXYLAMINE

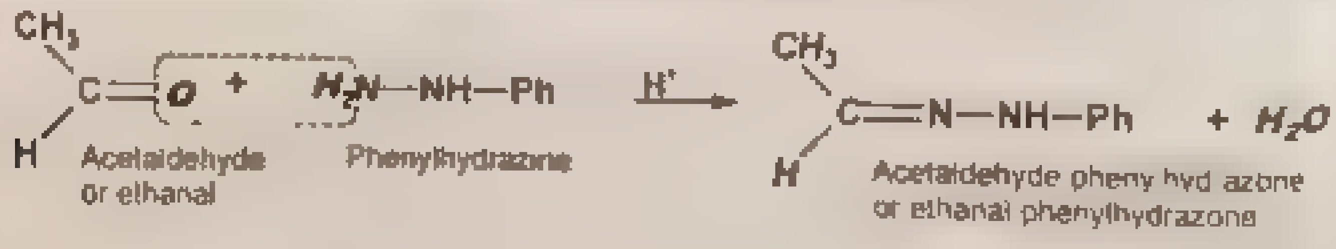
Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.

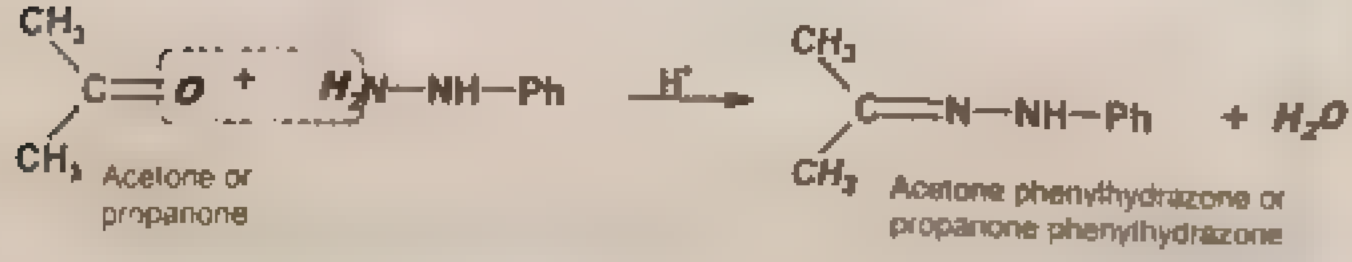




REACTION WITH PHENYLHYDRAZINE

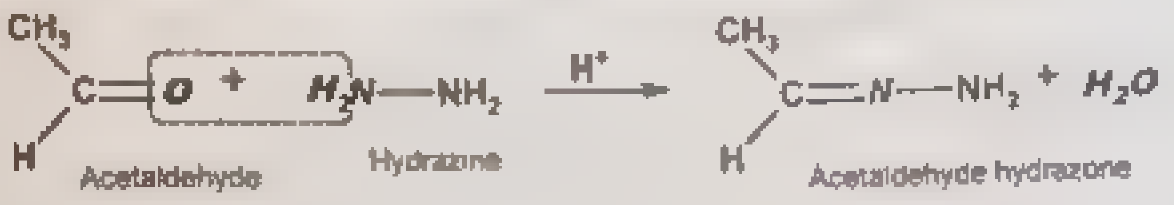
Aldehydes and ketones react with phenylhydrazine to form phenylhydrazones in the presence of an acid.

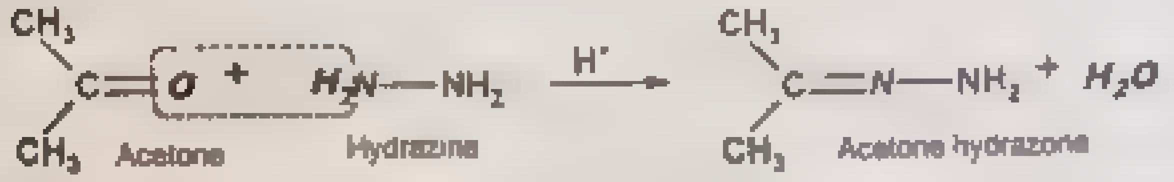




REACION WITH HYDRAZINE

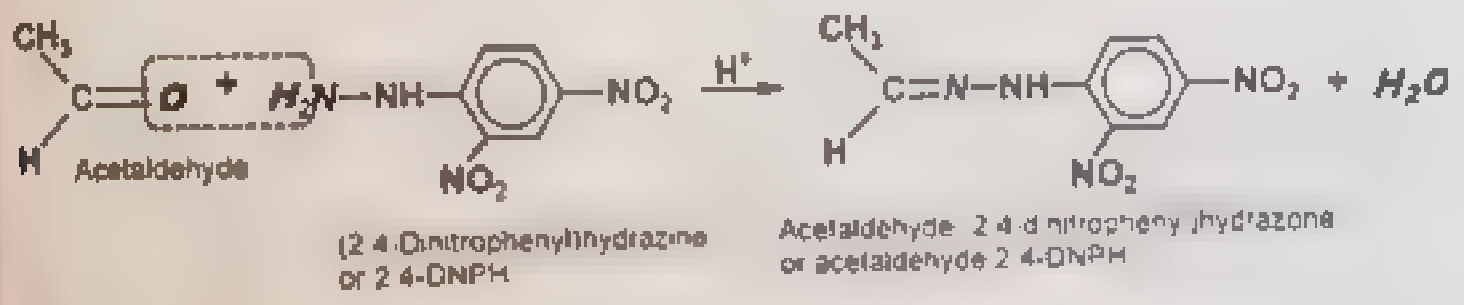
Aldehydes and ketones react with hydrazine to form hyrazones in the presence of an acid

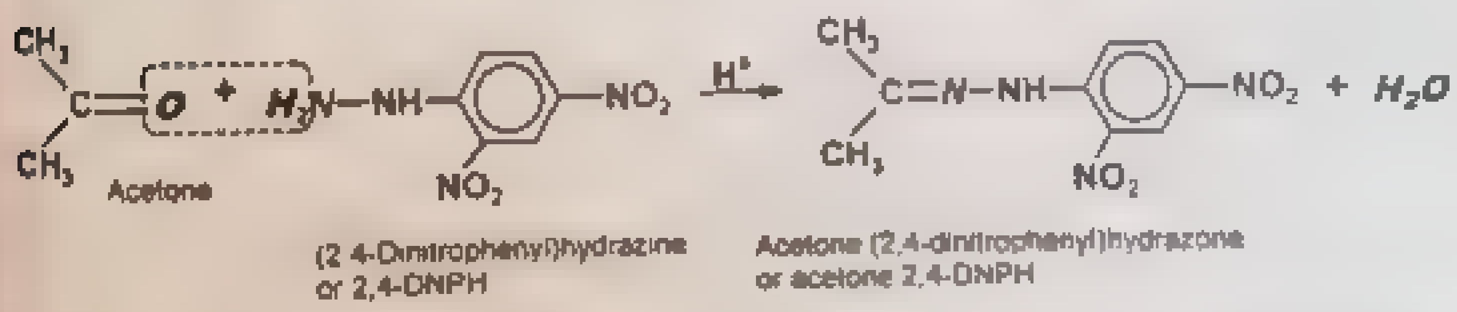




REACTION WITH 2,4-DINITROPHENYLHYDRAZINE

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazone in the presence of an acid



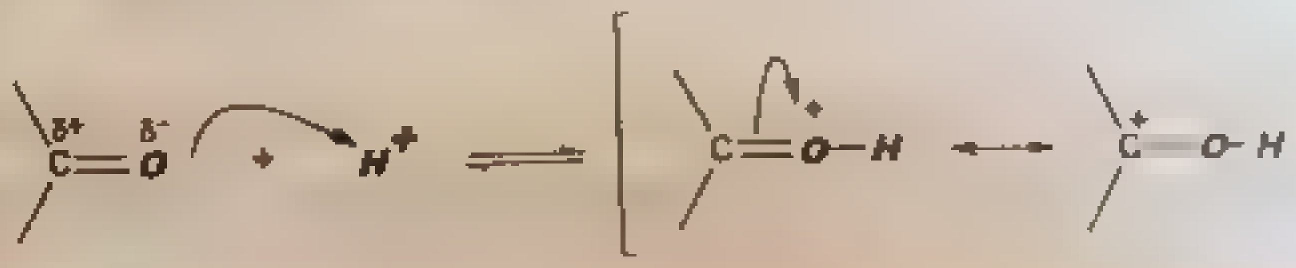


The reaction can be used for the identification of aldehydes and ketones because 2,4-dinitrophenylhydrazones are usually yellow or orange crystalline solids

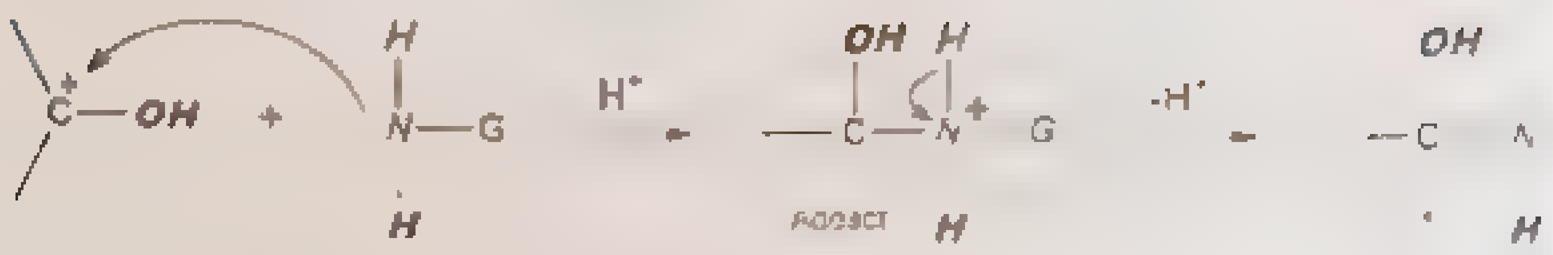
Exercise Q3 (vii) What is the mechanism for addition of ammonia derivatives to carbonyl group?

Mechanism of the Reaction of ammonia derivatives

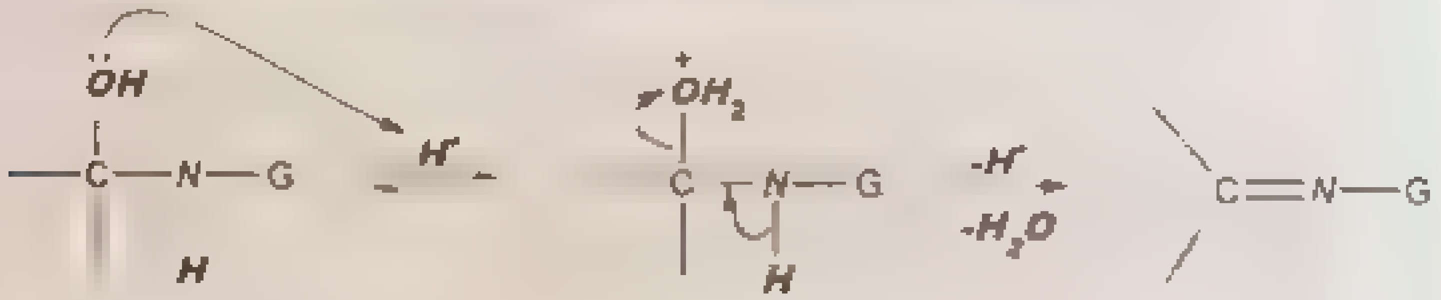
Step 1 Protonation of oxygen of the carbonyl group



Step 2



Step 3



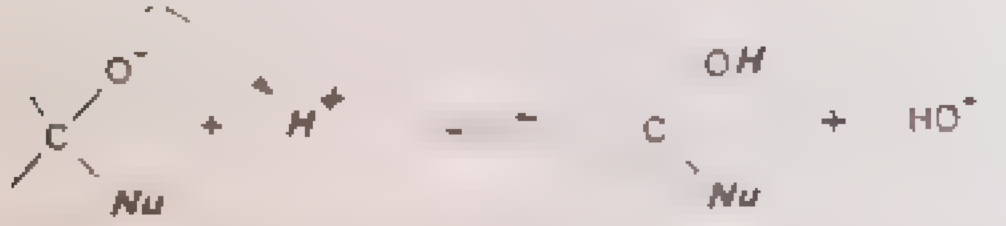
(3) ADDITION OF ALCOHOLS

Aldehydes combine with alcohols in the presence of ... chloride acts as a catalyst

The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To rege... aldehyde, the acetal is hydroelysed in the presence of an acid

Note Ketones do not react under these conditions

RELATIVE REACTIVITY OF ALDEHYDES AND KETONES



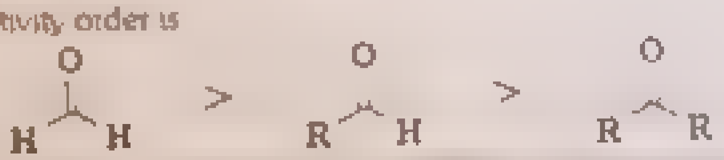
The reac... contributor which has char... ve O. In general the reactivity ... aldehydes > ketones ...

The substituents ...

(1) *Size of the substituent* ... Larger groups ... nucleophile

(2) *The electronic effect* ... Alkyl groups ... electrophilic and therefore less ...

Thus the reactivity order is



These trends are supported by the trends in the equilibrium data ... ation of hydrate

Carbonyl	K (M)	% Hydrate
methanal	41	99.96
ethanal	1.0 x 10	[illegible]
2,2 dimethyl propanal	4.1 x 10	19
propanone	2.5 x 10	0.14

$K = [\text{hydrate}]/[C{=}O]$

Thus, methanol has high value of K, so its equilibrium is appreciably goes to the right. Hence ...

REDUCTION OF ALDEHYDES AND KETONES

REDUCTION TO HYDROCARBONS

Clemmensen Reduction (acidic conditions)

- Zn(Hg) in HCl reduced the C=O into CH_2

Wolff-Kishner Reduction (basic conditions)

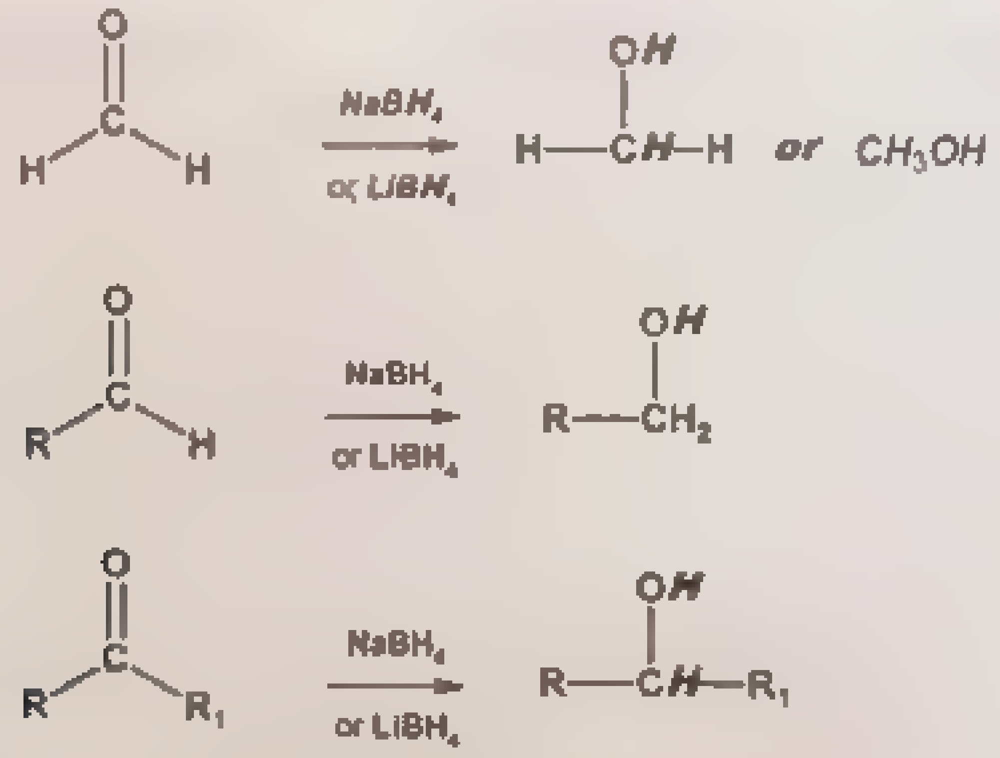
- NH_2NH_2, KOH, ethylene glycol (a high boiling solvent) reduces the C=O → CH_2

Overview

- These reduction methods do not reduce C=C, C≡C or CO_2H
- The choice of method should be made based on the tolerance of other functional groups to the acidic or basic reaction conditions

HYDRIDE REDUCTIONS OF ALDEHYDES AND KETONES

Hydride reacts with the carbonyl group, C=O, in aldehydes or ketones to give alcohols.



- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents $LiAlH_4$ and $NaBH_4$ act as a source of 4H (hydride ion)
- Overall 2 H atoms are added across the C=O to give H-C-O-H.
- The substituents on the carbonyl tell the nature of the product alcohol
- Reduction of methanal (formaldehyde) gives methanol.
- Reduction of other aldehydes gives **primary** alcohols.
- Reduction of ketones gives **secondary** alcohols.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid base reaction

CLASSIFICATION SUMMARY OF REACTIONS OF CARBONYL COMPOUNDS WITH DIFFERENT NUCLEOPHILES

(1) USING CARBON NUCLEOPHILES

CYANOHYDRIN FORMATION

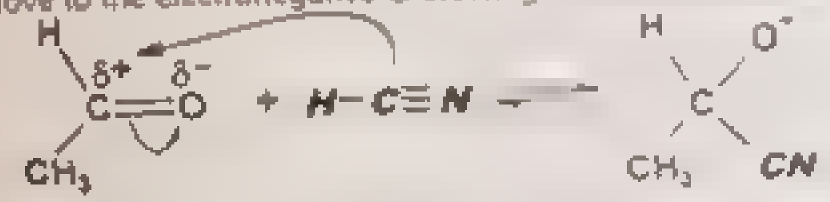
- Cyanide adds to aldehydes and ketones to give a cyanohydrin.

- The [illegible]
- HCN is a fairly weak acid, but ***very toxic***
- The reaction is useful since [illegible] or $-CH_2NH_2$

NUCLEOPHILIC ADDITION OF CYANIDE TO AN ALDEHYDE

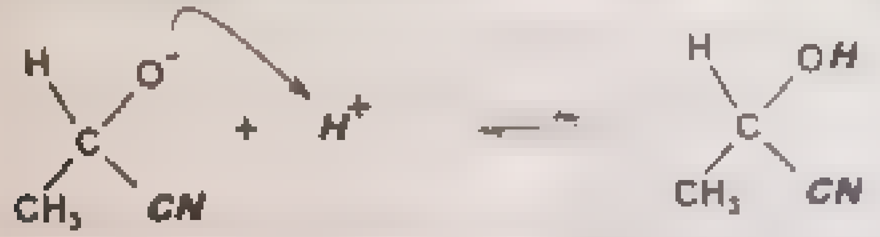
Step 1:

The nucleophilic C in the cyanide adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an [illegible]



Step 2.

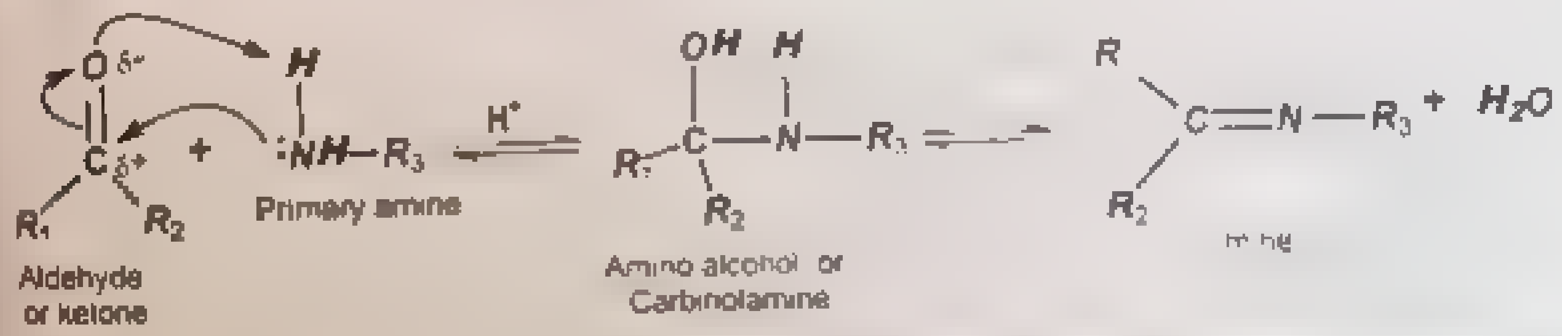
An acid/base reaction. [illegible]



(2) USING NITROGEN NUCLEOPHILES

Reactions of Primary Amine derivatives

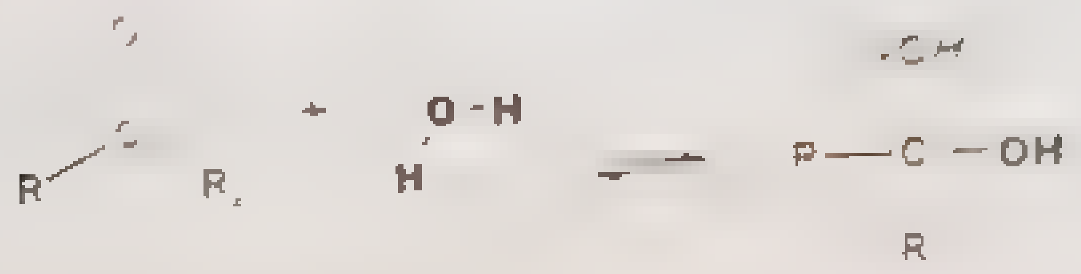
Primary amines **R-NH$_2$** or **ArNH$_2$** undergo [illegible] to give **carbinolamines** which then dehydrate to give substituted **imines**



- The reactions are usually carried out in an acidic buffer to activate the C=O and [illegible] dehydration but without inhibiting the nucleophile
- Systems of the general type **H$_2$N-G** undergo this type of reaction and can be used

(3) USING OXYGEN NUCLEOPHILES

Formation of Hyd... hydrates



- In general ...
- However ...
- Understand ...

MECHANISM FOR THE ACID catalyzed FORMATION OF HYDRATES

Step 1

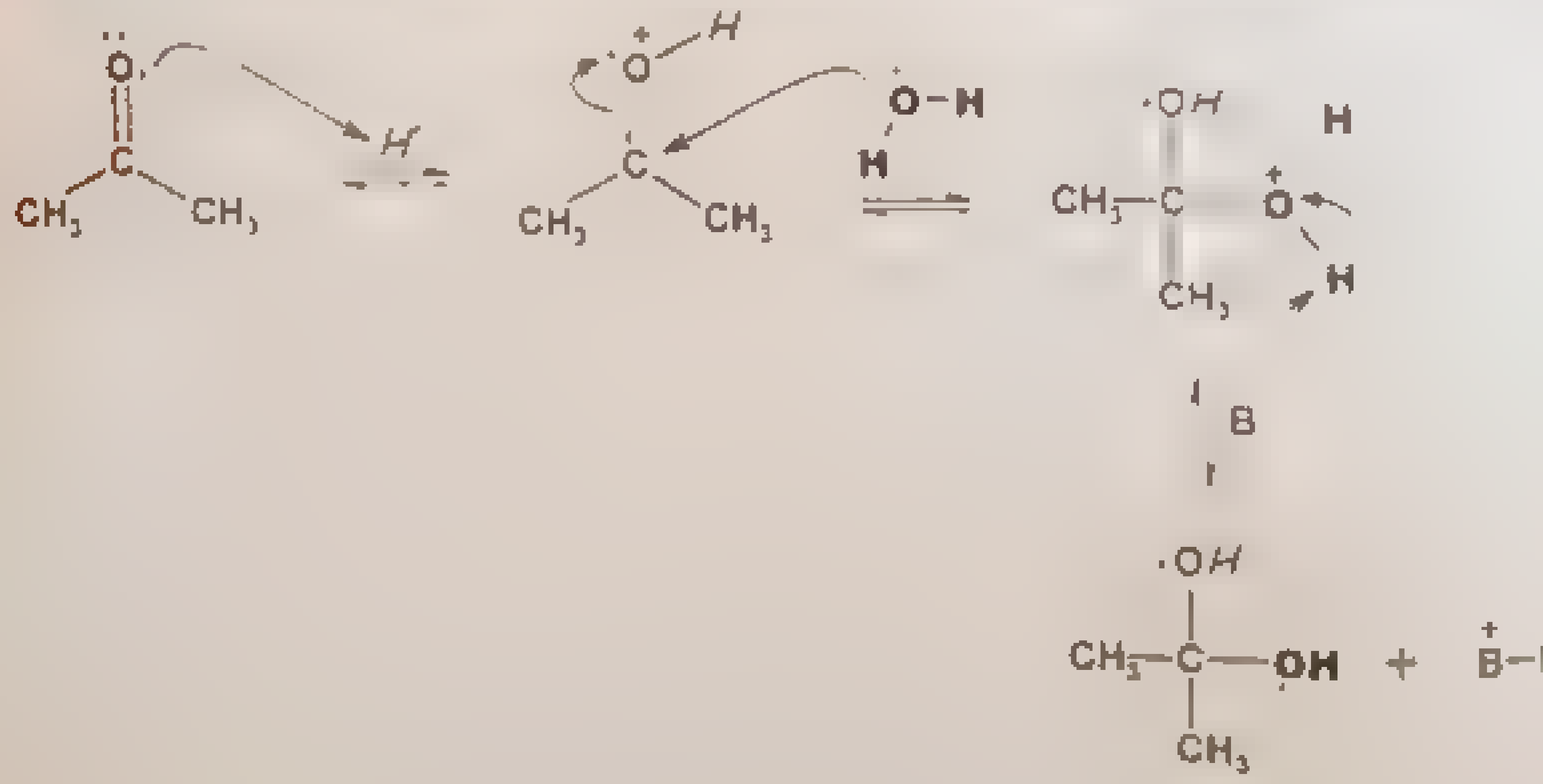
An acid/base reaction. Since there is ... protonating on O

Step 2

The nucleophilic O ... electrons to the positive O

Step 3

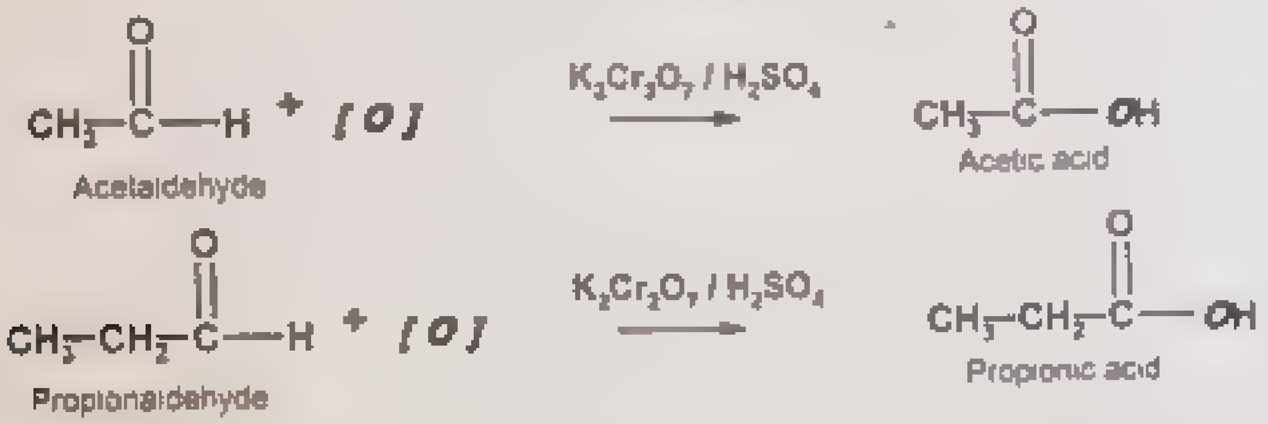
An acid/base reaction. Deproto...



OXIDATION REACTIONS

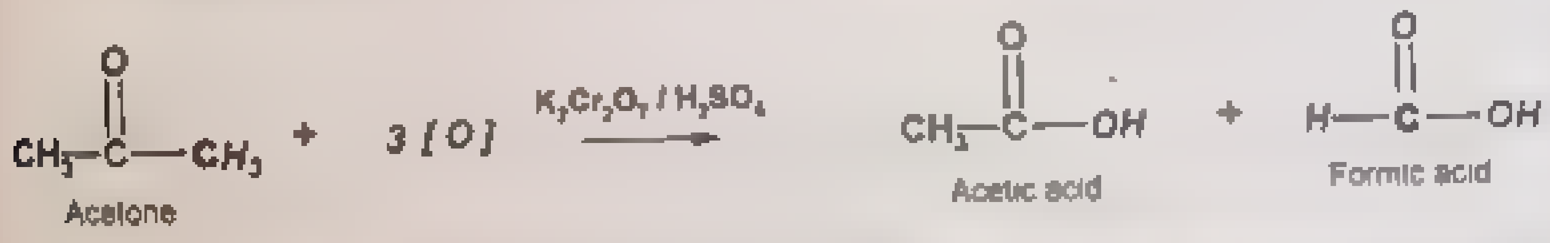
OXIDATION OF ALDEHYDES

- Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids.
- They are also oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$, and dilute nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group in these reactions.

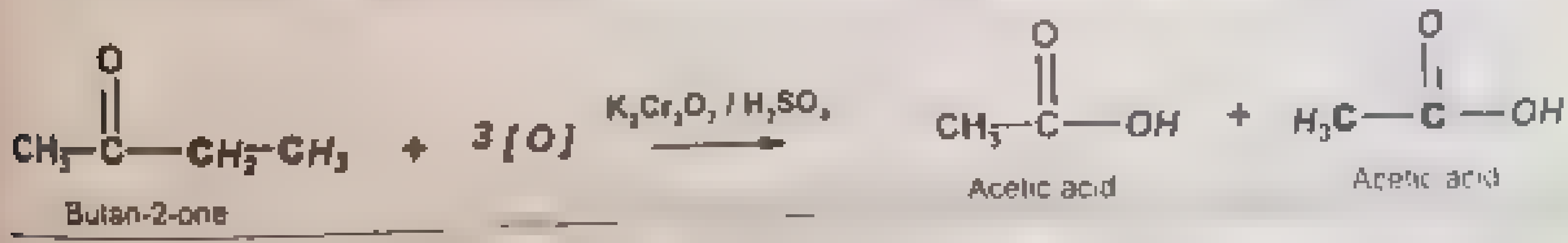


OXIDATION OF KETONES

- Ketones are only oxidized by strong oxidizing agents such as $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$ and conc. HNO_3.
- The carbon atom joined to the smaller number of hydrogen atoms is oxidized.
- In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized. And mixture of two carboxylic acids is always obtained.

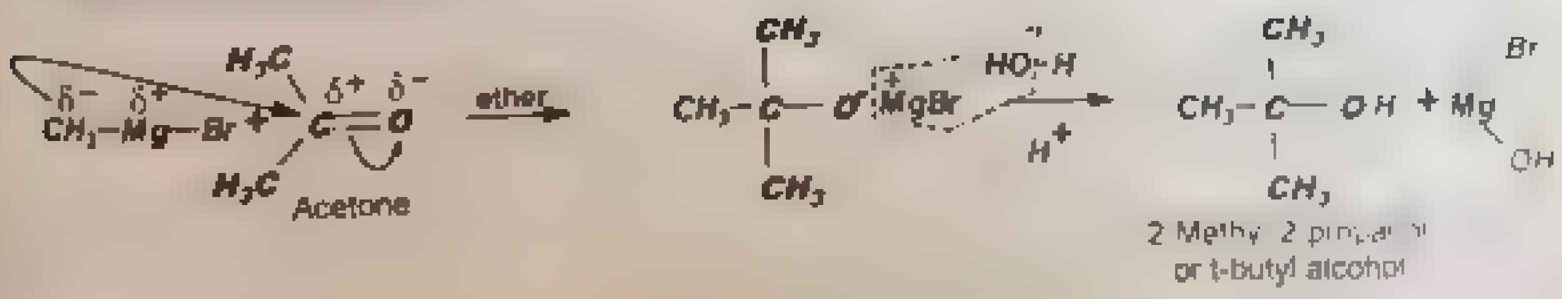


- However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



SOME IMPORTANT CONVERSIONS

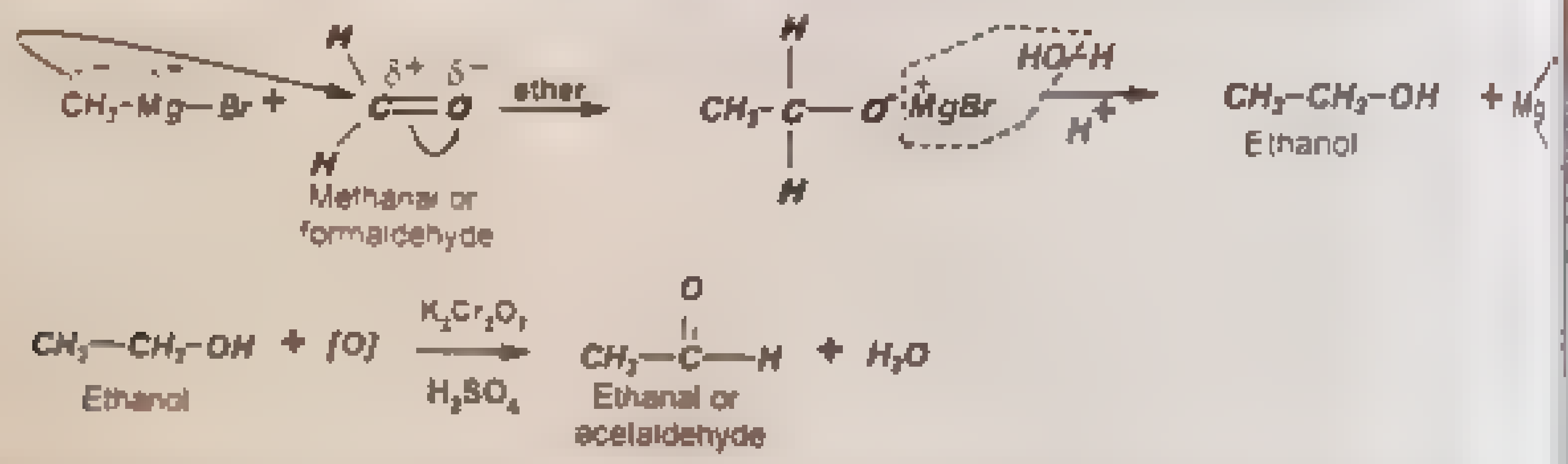
(i) Acetone into t-butyl alcohol



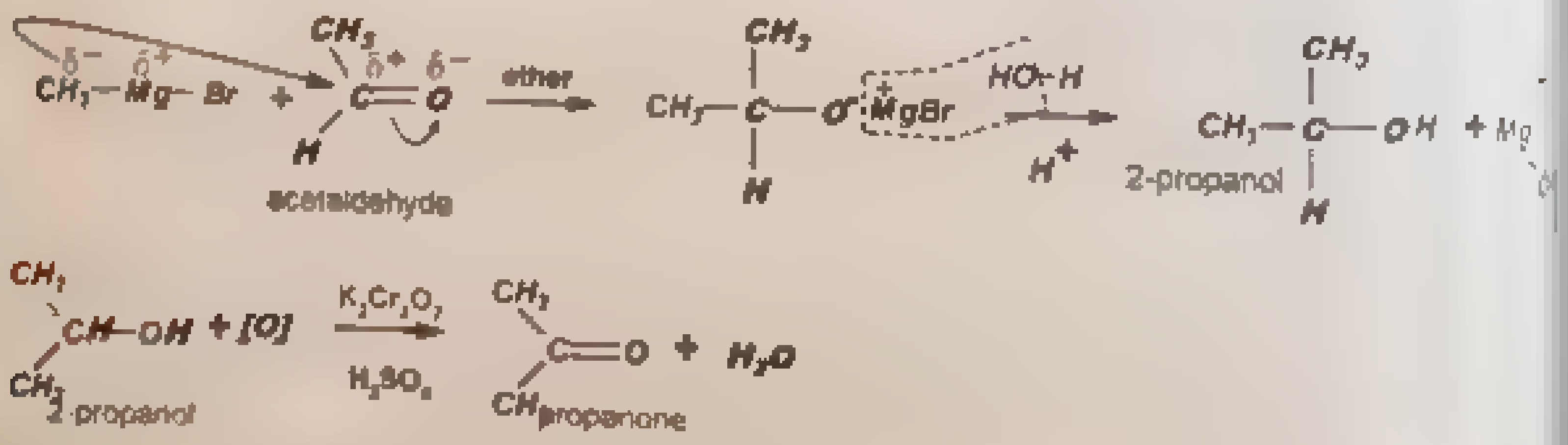
(ii) Propanal into 1-propanol

(iii) Propanone into 2-propanol

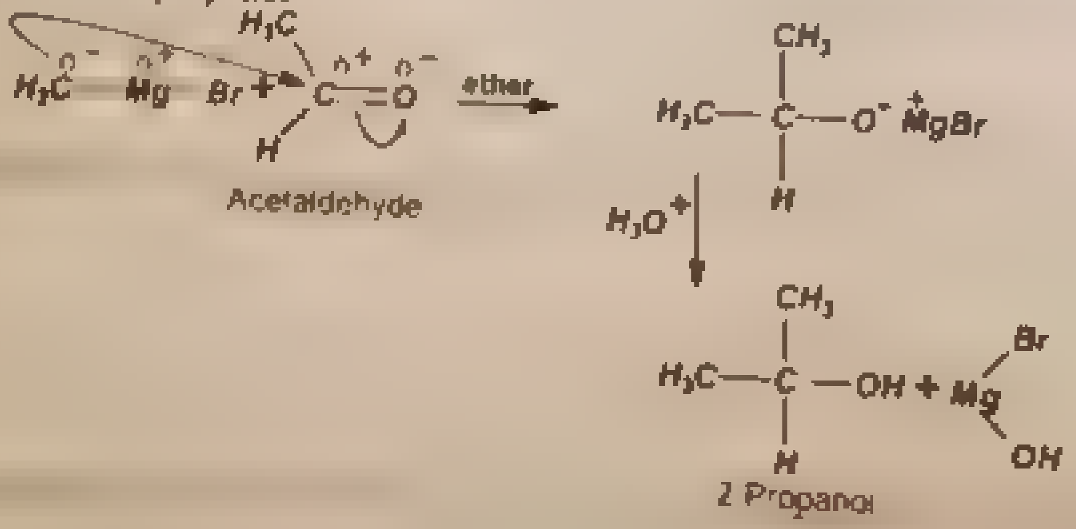
(iv) Methanal into ethanal



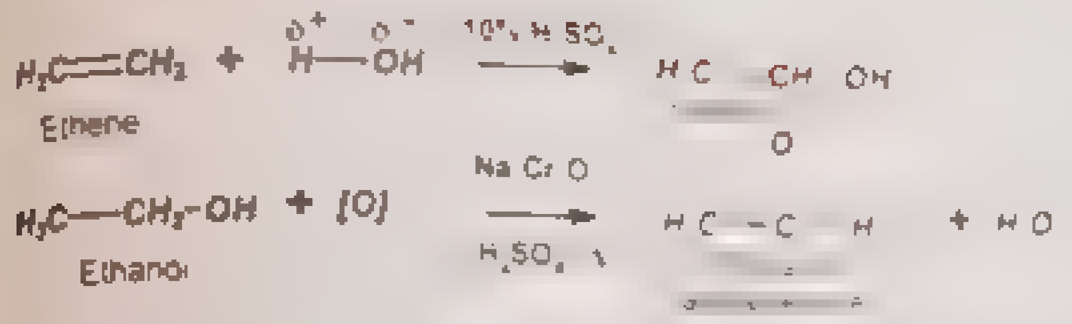
(v) Ethanal into propanone



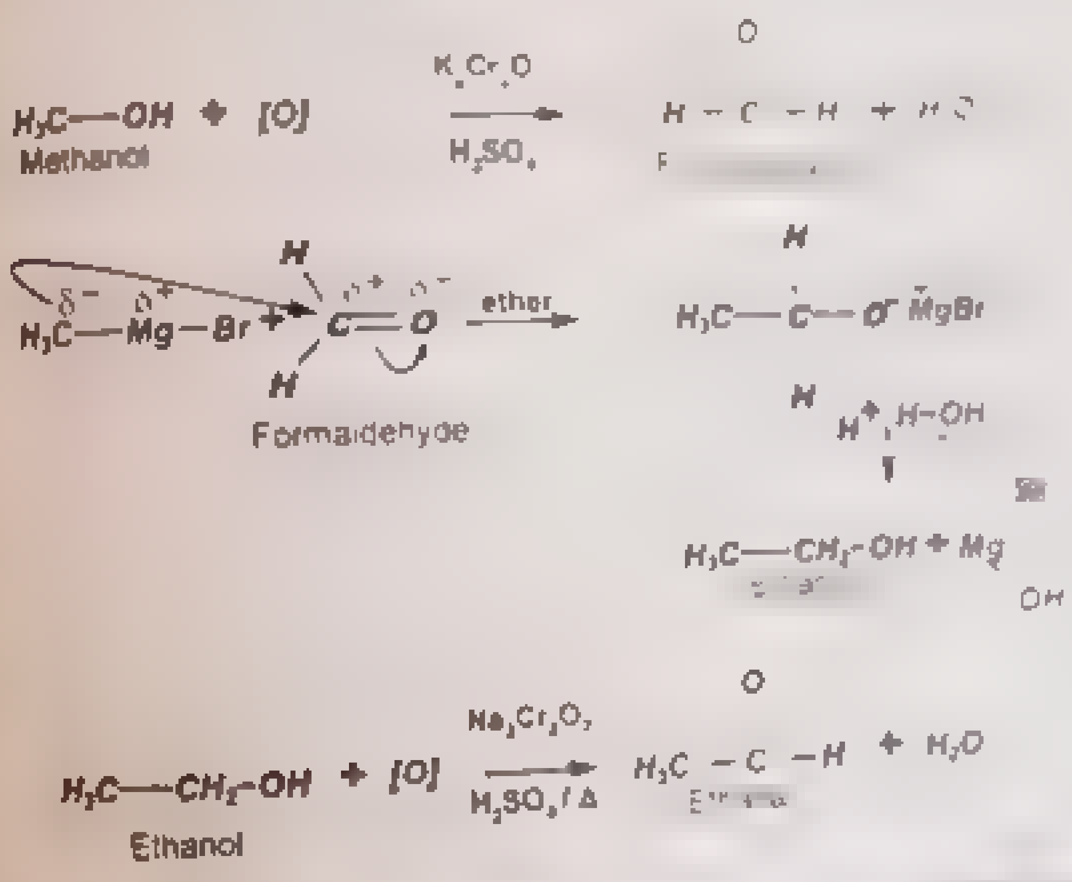
(vi) Ethanal into 2-propanol



(ii) Ethene into ethanal



(iii) Methanol into ethanal



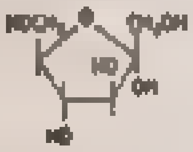
SOCIETY, TECHNOLOGY AND SCIENCE

Sugars Glucose and Fructose – *Naturally occurring carbonyl compounds*

- Sugars are sweet tasting soluble carbohydrates
- Carbohydrates derive their name for the fact that ... H and O in the ratio of 2 : 1 as in water
- Monosaccharides such as glucose are usually ... their molecules.
- Disaccharides such as sucrose consist of two monosaccharide ... molecule of water
- Polysaccharides such as starch are made up of many ... Monosaccharides all have asymmetric molecules ...
- The most obvious feature of the structure of the Monosaccharides ... number of –OH groups. These give them a large capacity ... solids, soluble in water. The presence of –OH groups ... thought to be responsible for the sweet taste of sugars
- The most obvious feature of the structure of the Monosaccharides ... number of –OH groups. These give them a large capacity for ... soluble in water

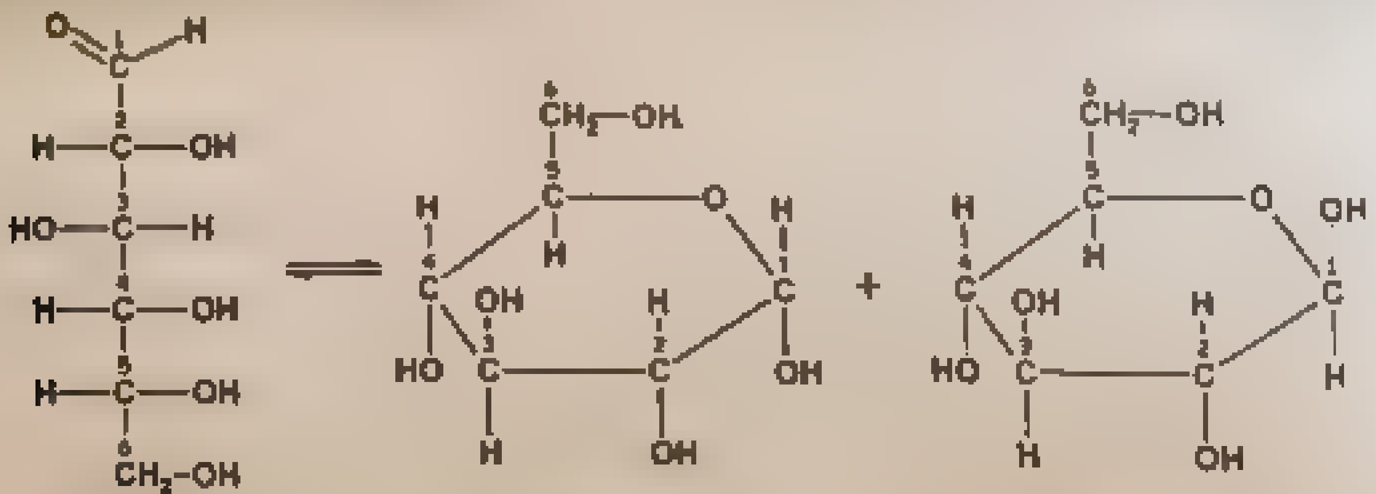
- The presence of –OH groups on several adjacent ca[illegible] for the sweet taste of sugars
- Sugars also show many properties in s[illegible] gives a crystalline condensation compound [illegible] structure of glucose contains no carbonyl gr[illegible]

Some common carbohydrates. In the ring structures, the C atoms in the ring and the H atoms attached to them have been omitted, for clarity

Name	Type	Structure	Occurrence
glucose	monosaccharide, aldose, hexose	 (this is α-glucose: see section 9.3 for details of α- and β-glucose)	occurs abundantly in plants and animals
fructose	monosaccharide, ketose, hexose		in fruit and honey
ribose	monosaccharide, aldose, pentose		component of the molecules of ribonucleic acid (RNA) and vitamin B12
sucrose	disaccharide	glucose — fructose	sugar cane, sugar beet (commonly simply called 'sugar')
maltose	disaccharide	glucose — glucose	malt
lactose	disaccharide	glucose — galactose	milk
starch	polysaccharide	chains of glucose units	plant storage organs, e.g. potato, wheat grain
cellulose	polysaccharide	chains of glucose units (linked differently to those in starch)	structural material of plants

The carbonyl properties possessed by glucose arise from the fact that in addition to its normal ring form [illegible] exist as an open chain form.

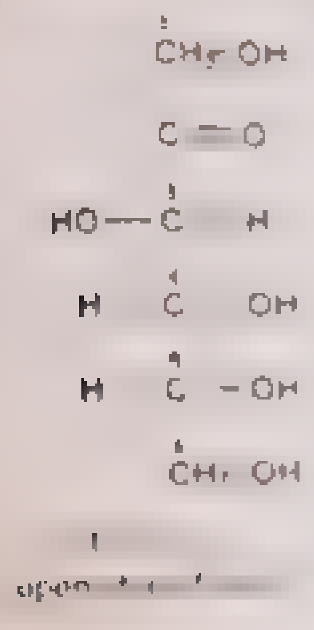
Glucose – An example of aldehyde

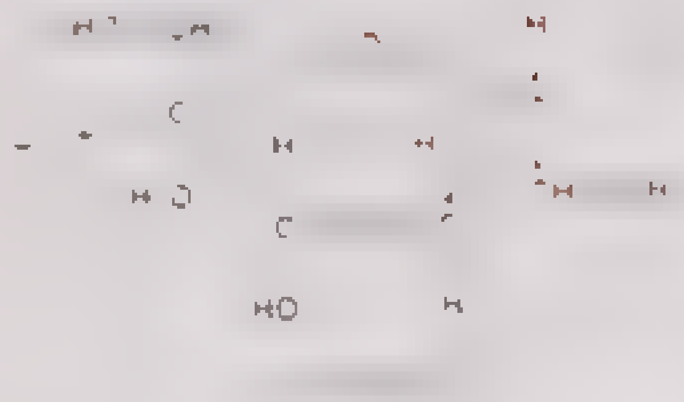


D-Glucose (open chain form) α-D-Glucose β-D-Glucose (cylic form)

- The two forms are readily inter-converted and in aqueous solution about 1% of glucose molecules [illegible] in the open chain form.

Fructose - An example of Ketone





Why does the open chain form of glucose and other sugars change ...

It is a result ... involved is the ... addition reaction ...

DO YOU KNOW?

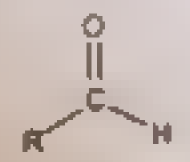
- 40% aqueous ...
- *Acetone is widely used as ...*
- *Formaldehyde is used as ...*
- *Formaldehyde is used in ...*

QUICK QUIZ-2

(1) What is functional group of carbonyl compounds. Write their general formula ...

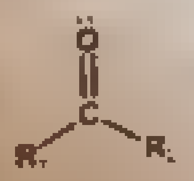
Carbonyl compounds are aldehydes a... The compound in which carbonyl group ... aldehydes

Their general formula is



The compounds in which carbonyl group is direct... compounds C = O group occurs within chain ...

Their general formula is



where R_1 and R_2 ...

(2) What types of aldehydes used in Cannizzaro's reactions

Aldehydes having no α-hydrogen atoms undergo Cannizzaro's reaction

e.g. Formaldehyde, HCHO · Benzaldehyde C_6H_5CHO etc

(3) What is Cannizzaro's reaction?

- Aldehydes having no α-hydrogen atoms undergo Cannizzaro's reaction
- It is a disproportionate (self oxidation-reduction) reaction
- Two molecules of the aldehyde are involved. One molecule is reduced into corresponding ... the other is oxidized into the acid (in the salt form)
- The reaction carried out with 50 % aqueous solution of sodium hydroxide at room temperature

(4) Which types of carbonyl compound condense to form an aldol?

Aldehydes having at least one α-hydrogen atoms undergo Aldol Condensation reaction

e.g. Acetaldehyde, CH_3CHO etc.

(5) What is haloform reaction?

Acetaldehyde, ethanol, methyl ketones and secondary alcohols with methyl group at α carbon react with halogens (Cl_2, Br_2, I_2) in the presence of sodium hydroxide to give haloform (chloroform, bromoform, iodoform) and sodium salt of the acid. This reaction is called haloform reaction

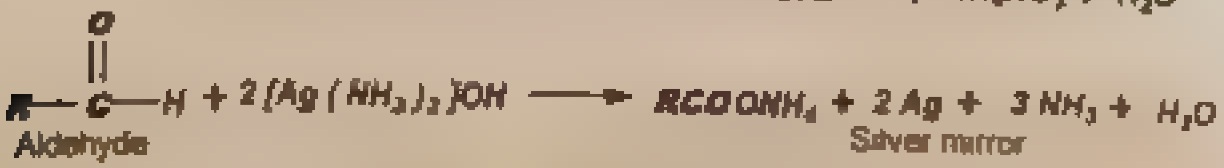
(6) Give the oxidation of reactions of aldehydes

- Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution oxidize aldehydes to carboxylic acids
- They are also oxidized by strong oxidizing agents such as $K_2Cr_2O_7$ / H_2SO_4, $KMnO_4$ / H_2SO_4 or nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to ... reactions

(7) Give the reactions of aldehyde with tollen's reagent

- Aldehydes form silver mirror with Tollen's reagent (ammonical silver nitrate solution)
- Add Tollen's reagent to an aldehyde solution in a test tube and warm
- A silver mirror is formed on the inside of the test tube

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + H_2O$$



(i) *What types of ppt. are formed when aldehyde reacts with Fehling's solution*

- A ... red ...
- To an aldehyde solution, add Fehling's solution and boil.
- A brick-red precipitate of cuprous oxide is formed.
- Ketones do not give this test.

$$\underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + 2\,Cu(OH)_2 + NaOH \xrightarrow{\text{boil}} RCOONa + \underset{\text{Brick red ppt}}{Cu_2O} + 3\,H_2O$$

KEY POINTS

- Primary alcohols can be oxidized ... acids.
- Secondary alcohols can be oxidized to ketones.
- Tertiary alcohols cannot be oxidized (no carbinol C-H).
- The protonation of a carbonyl gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.
- Organolithium or Grignard reagents react with the carbonyl group ... ketones to give alcohols.
- The carbonyl group (C=O) is present in aldehydes and ketones. In aldehydes it is in a terminal position in the carbon chain. In ketones it is in a non-terminal position.
- Aldehydes and ketones are named ...
- Aldehydes are prepared by ... alcohols, ketones ...
- The carbonyl group ... a molecule of water, resulting in a condensation reaction.
- Aldehydes are generally more reactive than ketones.
- The tendency of aldehydes to undergo nucleophilic addition ...
- Aldehydes can be oxidized to carboxylic acids by ...
- The carbonyl group activates the hydrogen atoms ... substituted than those in alkanes.

EXERCISE

Q1: Select the right answer from the choices given with each question.

(i) The carbon atom of a carbonyl group is

(a) sp hybridized (b) sp^2 hybridized ... (d) none of these

(ii) Ketones are prepared by the oxidation of

(a) Primary alcohol (b) Secondary ...

(iii) Acetone reacts with HCN to form a cyanohydrin. It is an example of

(a) Electrophilic addition (b) ...
(c) Nucleophilic addition (d) Nucleophilic substitution

(iv) Cannizzaro's reaction is not given by

(a) Formaldehyde (b) Acetaldehyde (c) Benzaldehyde (d) Trimethylacetaldehyde

(v) Which of the following reagents will react with both aldehydes and ketones?

(a) Grignard reagent (b) Tollen's reagent ...

(vi) Aldehydes are the oxidation product of

(a) p-alcohols (b) s-alcohols (c) ter alcohols (d) carboxylic acids

(vii) Which of the following compounds will not give iodoform test on treatment with I_2/NaOH

a) Acetaldehyde (b) Acetone ...

(viii) Aldehydes and ketones are carbonyl compounds. Which of them react both with $NaBH_4$ and with Tollen's reagent.

(a) Both aldehydes and ketones (b) Aldehydes only

(c) Ketones only (d) Neither aldehydes [illegible]

(ix) *Which one of the following can undergo Aldol condensation reaction?*

(a) Formaldehyde [illegible]

(x) *Aldol condensation is not successful with compounds*

(a) Having no α hydrogen (b) Having α hydrogen [illegible]

(xi) *Phenylhydrazine on treatment with carbonyl compounds with*

(a) Hydroxyl amines (b) Phenylhydrazone [illegible]

(xii) *Formaldehyde react with NH_3 to give?*

(a) Tetra ethylene hexamine (b) tetra ethylene tetramine

(c) Hexa methylene tetramine [illegible]

(xiii) *General formula of aldehyde and ketone is?*

(a) $C_nH_{2n}O$ (b) $C_nH_{2n+1}O$ (c) C_nH_nO [illegible]

(xiv) *Which of the following can be prepared in the laboratory by dry distillation of $(HCOO)_2Ca$?*

(a) $H_2C=CH_2$ [illegible] CH_3OH [illegible]

(xv) *The colour of Iodoform is*

(a) White (b) Black (c) Yellow (d) Blue

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (b) sp^2 hybridized

The carbonyl carbon is sp^2 [illegible] hybridized orbitals for sigma bonds [illegible] unhybridized $2p_z$ orbital for pi bond [illegible]

(ii) Ans: (b) Secondary alcohol

$$(CH_3)_2CH-OH + [O] \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} (CH_3)_2C=O + H_2O$$

(iii) Ans: (c) Nucleophilic addition

Since CN^- from HCN acts as a nucleophile [illegible] carbonyl carbon. So HCN addition is a nucleophilic addition [illegible]

(iv) Ans: (b) Acetaldehyde

[illegible]

(v) Ans: (a) Grignard reagent

Grignard's reagent reacts with both aldehydes and ketones to produce alcohols

(vi) Ans: (a) p-alcohols

[illegible]

(vii) Ans: (d) 3-pentanone

Iodoform test is given by methyl ketones i.e. the ketones which have a methyl group adjacent to the carbonyl group. Since 3-pentanone has no methyl group adjacent to the carbonyl group, so it will not give iodoform test.

(viii) Ans: (b) Aldehydes only

Aldehydes are oxidised [illegible] Aldehydes are also [illegible] ketones are not oxidised by Tollen's [illegible]

(ix) Ans: (b) Acetaldehyde

Aldol condensation reaction is given by aldehydes which have α-hydrogen. Since acetaldehyde (CH_3CHO) has α-hydrogens so it will give Aldol condensation reaction

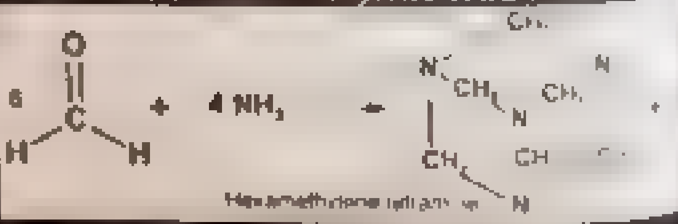
(x) Ans: (a) Having no α-hydrogen

Aldol condensation reaction is [illegible] which have α-hydrogen

(xi) Ans: (b) Phenylhydrazone

Phenyl hydrazine reacts with a carbonyl compound to give phenyl hydrazine

(xii) Ans: (c) Hexa methylene tetra amine



(xiii) Ans: (a) $C_nH_{2n}O$

Since, two hydrogen atoms are removed and one oxygen atom is added.

(xiv) Ans: (b) HCHO

$$(HCOO)_2Ca \xrightarrow{heat} HCHO + CaCO_3$$

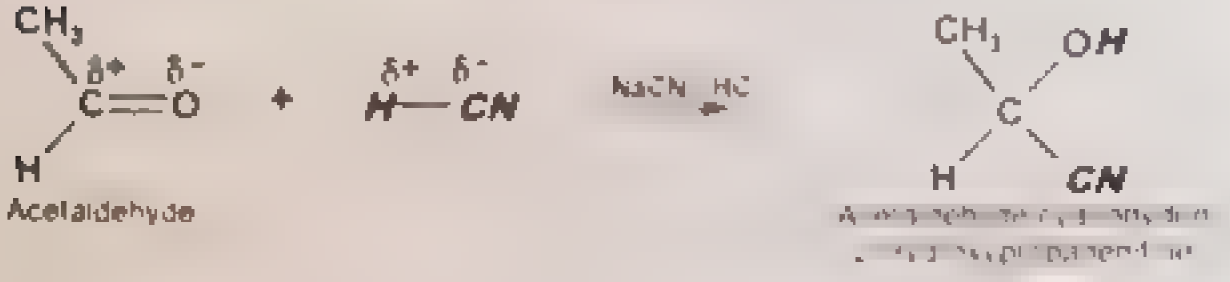
(xv) Ans: (c) Yellow

The colour of iodoform is yellow.

(iii) What is the mechanism of HCN addition to carbonyl compounds?

(iv) How is ethanol converted to lactic acid?

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + [O] \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3-\overset{O}{\overset{\|}{C}}-H} + H_2O$$



$$\underset{\text{2-Hydroxypropanenitrile}}{H_3C-\overset{OH}{\overset{|}{C}H}-CN} + 2H_2O + H_2SO_4 \longrightarrow \underset{\substack{\text{2-Hydroxypropanoic acid} \\ \textit{(Lactic acid)}}}{H_3\overset{3}{C}-\overset{OH}{\overset{|}{\overset{2}{C}H}}-\overset{1}{C}OOH} + NH_4HSO_4$$

(v) What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?

(vi) What is Haloform reaction?

Acetaldehyde, ethanol, methyl ketones and secondary alcohols with methyl group at ... react with halogens (Cl_2, Br_2, I_2) in the presence of sodium hydroxide to give haloform (chloroform ... or iodoform) and sodium salt of the acid. This reaction is called haloform reaction.

$$\underset{\text{R=Alkyl or aryl or H}}{R-\overset{O}{\overset{\|}{C}}-CH_3} + 3X_2 + 4NaOH \longrightarrow \underset{\text{Haloform}}{CHX_3} + \underset{\text{Sodium carboxylate}}{RCOONa} + 3NaX + 3H_2O$$

(vii) Which type of alcohols undergo Iodoform reaction?

Secondary alcohols containing the methyl group also undergo this reaction.

$$\underset{\text{Secondary alcohol}}{R-\overset{OH}{\overset{|}{C}H}-CH_3} + 4I_2 + 6NaOH \xrightarrow{\Delta} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium carboxylate}}{RCOONa} + 5NaI + 5H_2O$$

Ethanol is the only primary alcohol that gives this reaction.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + 4I_2 + 6NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{sodium formate}}{HCOONa} + 5NaI + 5H_2O$$

(viii) How are methanol and ethanol polymerized?

(ix) Why formaldehyde do not give aldol condensation reaction?

For aldol condensation reaction the carbonyl compound must have at least one α-hydrogen atom on the carbon atom next to carbonyl group. In formaldehyde there is no α-hydrogen so it cannot give aldol condensation reaction.

(x) Give the mechanism of addition of sodium bisulphate to ketones

Page 323

Q3: Give detailed answers for the following questions.

(i) What is the reactivity of the carbonyl group?

Page 319

(ii) How will you prepare formaldehyde and acetaldehyde on industrial scale?

In industry formaldehyde is prepared by passing a mixture of methanol vapours and air over iron oxide molybdenum oxide or Ag catalyst at 500°C

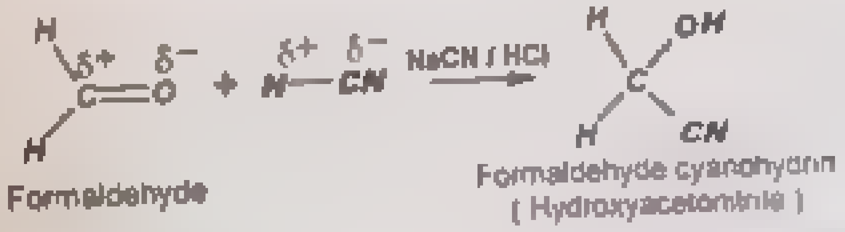
$$2\,CH_3OH + O_2 \xrightarrow[500^\circ C]{FeO,\ MoO_3} 2\,H-\overset{\overset{\large O}{\|}}{C}-H + 2\,H_2O$$

In industry acetaldehyde is prepared by oxidation of ethylene in air using palladium chloride catalyst with cupric chloride promotor

$$\underset{\text{Ethylene}}{2\,H_2C=CH_2} + O_2 \xrightarrow[H_2O]{PdCl_2 + CuCl_2} \underset{\text{Acetaldehyde}}{2\,H_3C-\overset{\overset{\large O}{\|}}{C}-H}$$

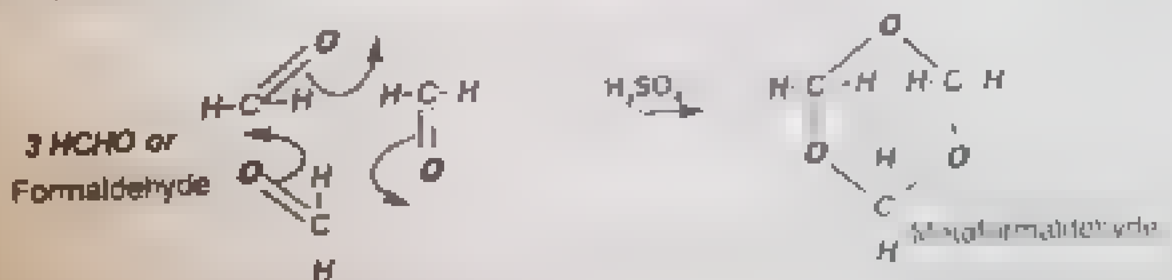
(iii) How formaldehyde reacts with following?

(a) HCN

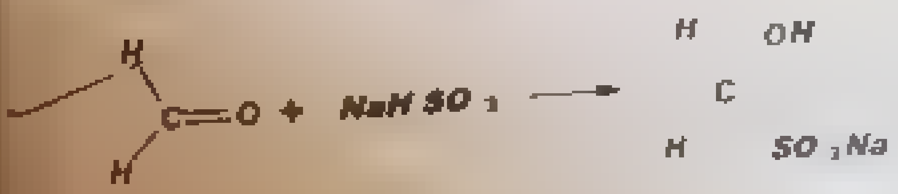


(b) H_2SO_4

Formaldehyde polymerizes in the presence of dil. H_2SO_4 to give metaformaldehyde



(c) $NaHSO_3$



(i) **Define and explain aldol condensation along with mechanism**
Page 324

(ii) **Give detail of haloform reaction. Why it is called so?**
Page 327

(iii) **Give the following reductions of aldehydes and ketones along with mechanism**
(a) $NaBH_4$ (b) Catalytic reduction
Page 333

(iv) **What is the mechanism for addition of ammonia derivatives to carbonyl group?**
Page 330

(v) **Which type of aldehydes give Cannizaro's reaction? Explain with mechanism**
Page 326

(vi) **How do you distinguish a ketone and an aldehyde by chemical method?**

Aldehydes gives silver mirror with Tollen's reagent while ketone does ...

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]OH \longrightarrow RCOONH_4 + 2Ag + 3NH_3 + H_2O$$

Aldehyde

Aldehydes gives red ppt with Fehling's solution ...

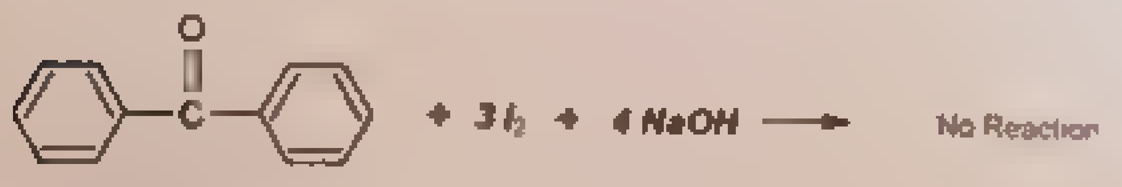
$$H_3C-\overset{O}{\overset{\|}{C}}-H + 2Cu(OH)_2 + NaOH \longrightarrow CH_3COONa + Cu_2O + 3H_2O$$

Ethanal

(vii) **How will you differentiate between acetophenone and benzophenone?**

Acetophenone is a methyl ketone so it will give iodoform test ...

Acetophenone Iodoform Sodium benzoate



Benzophenone

test

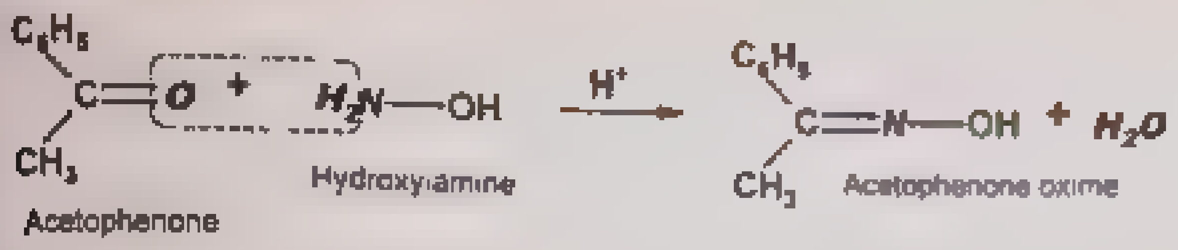
(viii) **Predict the formulas of the products of the following reaction**

(a) $CH_3COCH_2CH_3 + H_2 \rightarrow$

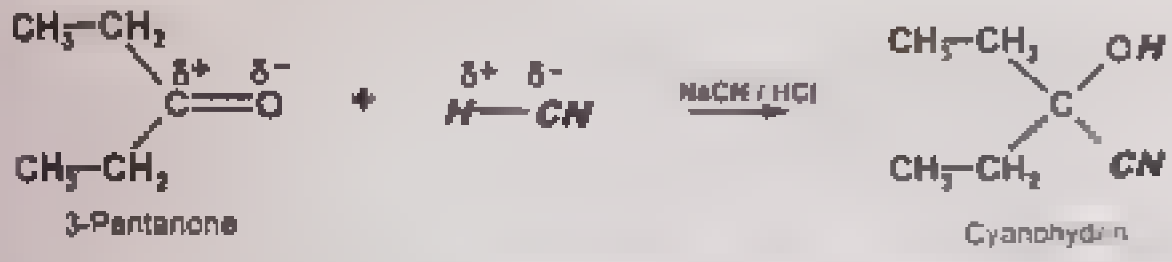
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 + H_2 \xrightarrow{Pd,\ Pt\ or\ Ni} CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_3$$

2-Butanone 2-Butanol

(b) $C_6H_5COCH_3 + NH_2OH \rightarrow$

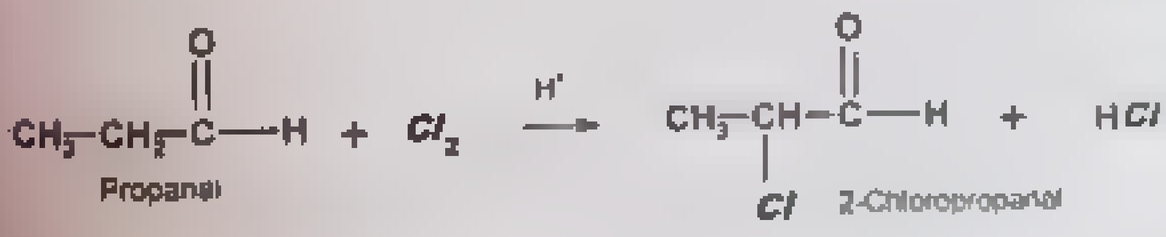


(c) $CH_3CH_2COCH_2CH_3 + HCN \rightarrow$

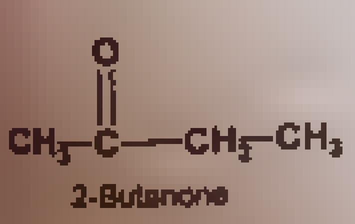


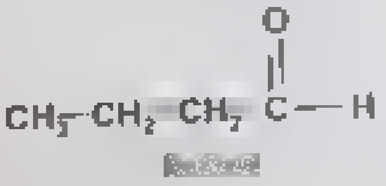
(d) $C_6H_5CHO + KMnO_4 \rightarrow$

(e) $CH_3CH_2CHO + Cl_2 \rightarrow$



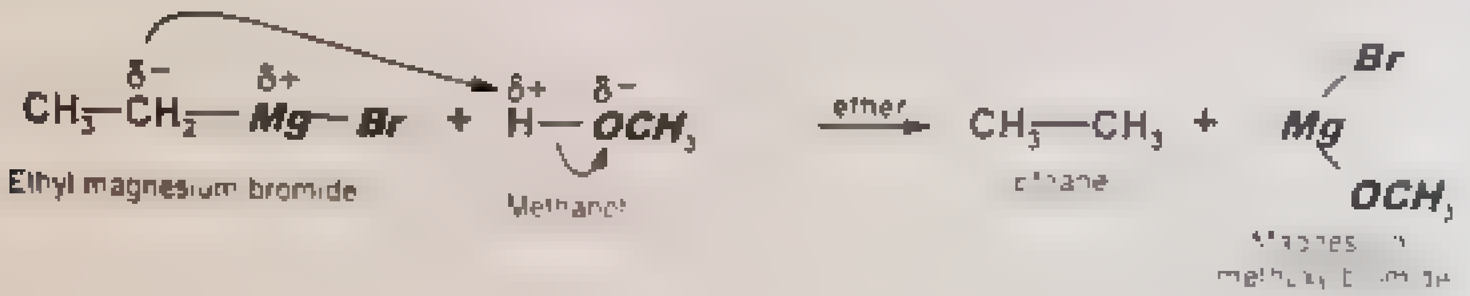
(xii) Write structural formulas for all compounds of molecular formula C_4H_8O containing a carbonyl group.





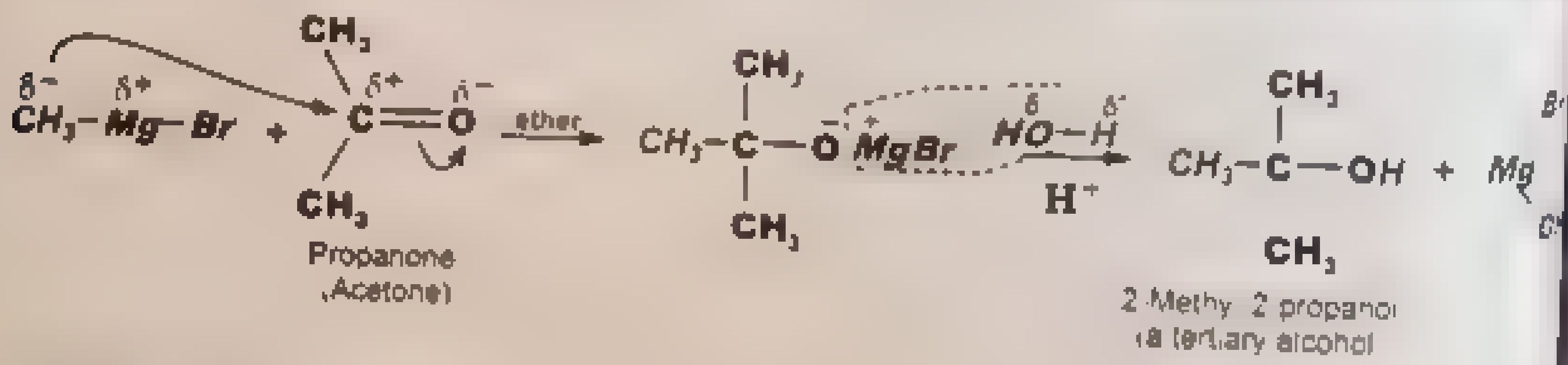
(xiii) Predicts the formulas of the compounds formed when the following are treated with the Grignard's reagent methyl magnesium bromide followed by water

Methanol

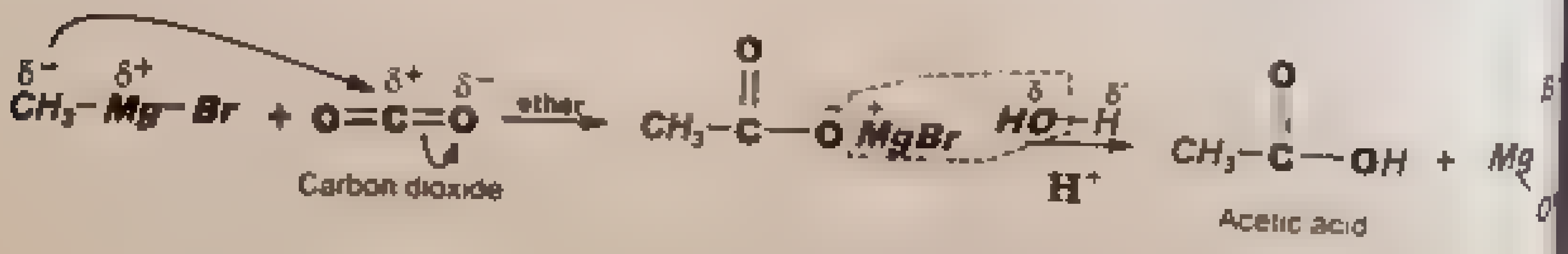


Ethanol

Propanone



Carbon dioxide



TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: **Over writing, cutting, erasing, using lead pencil will result in loss of marks**

Q1 Circle the correct option i.e. A/B/C/D. Each part carries one mark

(i) The carbon in carbonyl group is
A. sp^3 **B. sp^2** [illegible]

(ii) The name of formaldehyde in IUPAC system is
A. Ethanol B. Methanol **C. Methanal** [illegible]

(iii) Formalin is
A. 40% solution of CH_3CHO in water [illegible]
C. 40% solution of HCHO [illegible]

(iv) Which one of the following [illegible]
A. Formaldehyde **B. Acetaldehyde** [illegible]

(v) Aldehydes are more reactive than ketones because
A. [illegible] B. [illegible] **C. Both a and b** D. [illegible]

(vi) A cannizzaro's reaction takes place
A. With same molecule of aldehyde B. [illegible] of aldehydes
C. With same and different aldehydes D. [illegible]

(vii) Catalysts used for the preparation of formaldehyde [illegible]
A. [illegible] B. [illegible] C. [illegible] **D. All of above**

(viii) Aldol condensation is not successful with compound [illegible]
A. Having no α hydrogen B. [illegible] C. [illegible] D. None

(ix) Polymer of formaldehyde [illegible]
A. Meta formaldehyde B. Paraldehyde C. Both a and b D. None

(x) Tollen's test is used for the detection of
A. Aldehydes only B. [illegible] C. [illegible]

(xi) Aldol condensation [illegible]
A. Electrophilic [illegible] **B. Base catalyzed** C. [illegible]

(xii) Which of the following does not give iodoform reaction ?
A. CH_3CH_2OH **B. CH_3OH** C. CH_3CHO

(xiii) Phenylhydrazine on treatment with carbonyl group form
A. Phenyl hydrazones B. Hydroxyl amines C. Oximes

(xiv) acetals and ketals are formed by reaction of carbonyl compounds with
A. Acids **B. Alcohols** C. Phenols

(xv) Paraldehyde is a polymer of
A. Acetaldehyde B. Formaldehyde C. Propionaldehyde D. None

(xvi) isopropanol on [illegible]
A. Acetone B. [illegible] C. [illegible] **D. Propene**

(xvii) Which one of the following can undergo Aldol condensation [illegible]
A. Formaldehyde **B. Acetaldehyde** C. [illegible]

SUBJECTIVE

Total Marks Section B and C: 68

Time: 2.35 Hours **Section – B (Marks 42) (14 × 3 = 42)**

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines

(i) The reactions in which two molecules combine to form new compounds with or without [illegible]
Condensation
a. What type of condensation will be shown by the following
A. CH_3CHO B. C_6H_5CHO
b. Write chemical equation along with mechanism for the conversion of CH_3CHO into products [illegible]

(ii) a. Why the aldehydes with no α-hydrogen give Cannizzaro's reaction
b. Distinguish between benzaldehyde and acetaldehyde

(iii) Show with the help of mechanism how acetaldehyde in the presence of strong base gives crotonaldehyde 03

(iv) a. Write the formula of 2,4 - Dinitrophenyl hydrazine and [illegible]
b. Give the mechanism of the reaction between formaldehyde and [illegible]

(v) Give a reaction example of disproportionation reaction of aldehyde.

(vi) Give a general mechanism for the base-catalysed nucleophilic addition reaction of carbonyl 03

a. What is Tollen's test? Also give the reaction
b. Convert acetone → acetone hydrazone

a. Briefly explain the reactivity of carbonyl group
b. How can acetaldehyde be prepared by the dry distillation of a mixture having calcium salt of

a. What is the difference between an aldehyde and ketone?
b. What is formalin. How it can be obtained?

x. a. Discuss the reactivity of carbonyl group
b. What type of reactions aldehydes and ketones usually under go

xi. a. How α hydroxy acids are obtained from aldehydes and ketones?
b. What is a haloform reaction? Give one example

xii. a. What kind of aldehydes and ketones give aldol condensation gives an example of each?
b. What kind of aldehydes give cannizzaro's reaction?
c. Which aldehydes and ketones give haloform reactions?

xiii. a. What are acetals and how are they formed?
b. Why ketones do not undergo oxidation easily?

xiv. a. Distinguish between ethanol and Propanone by a chemical test
b. How will you distinguish between ethanal and propanal?

xvi) a. Describe briefly the mechanism of acid catalysed nucleophilic addition to a carbonyl

b. What is Fehling's solution test? Give chemical equation

(xvi) a. Give three industrial uses of formaldehyde
b. Give three industrial uses of Acetaldehyde

(xvii)a. Give the mechanism of addition of addition of HCN to Acetone?
b. Write the applications of Iodoform test?

xviii a. Why formaldehyde do not give aldol condensation reaction?
b. Give general mechanism of addition of phenyl hydrazine to acetaldehyde? 01

(xix a. How may acetaldehyde be prepared on industrial scale?
b. What is Benedict solution test?

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

Q. 3 a. How will you prepare formaldehyde on industrial scale?
b. What is Cannizzaro's reaction? Write its mechanism 03
c. How formaldehyde reacts with following 03
(i) HCN (ii) H_2SO_4 (iii) $NaHSO_3$ 03
d. Define and explain aldol condensation along with mechanism

Q. 4 a. Write mechanisms of the following reactions 04
(i) Cannizzaro's reaction
(ii) Addition of sodium bisulphite to acetone 05
b. How does acetaldehyde react with the following

(i) CH_3MgI (ii) $K_2Cr_2O_7$, H_2SO_4 (iii) $NaHSO_3$ (iv) NaOH

c Give the following reductions of aldehydes and ketones along with mechanism 4

(i) $NaBH_4$ (ii) Catalytic reduction

5. a. How will you identify carbonyl compounds by?

(i) 2, 4-DNP test (ii) Sodium bisulphate test 3

b Consider the following series of reactions involving Ethanal then answer the questions which follow:

$$Y \xleftarrow{HCN} CH_3CHO \xrightarrow{2,4\text{-}DNPH} X$$

$$CH_3CHO \xrightarrow{NaBH_4} Z$$

(i) Draw the structural formula of the compound Y and Z

(ii) Describe the appearance of the compound X. Give its name. Give out the mechanism for the reaction of Ethanal with 2, 4-DNPH to produce compound X 05

c. Give a chemical test by which you could distinguish between Ethanal and Propanone 1

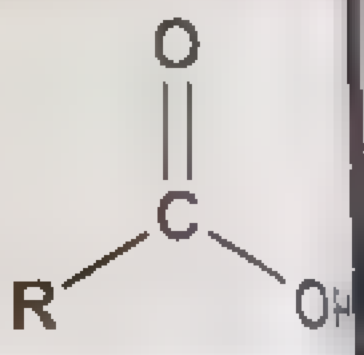
d How will you bring about the following conversions? 02

(i) Propanone into 2-Propanol

(ii) Methanol to propanoic acid

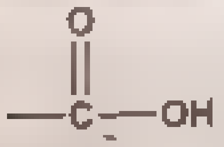
CHAPTER # 20

CARBOXYLIC ACIDS AND FUNCTIONAL DERIVATIVES

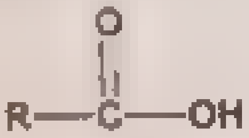


INTRODUCTION

- Organic compounds ... carboxyl group in their molecule are called carboxylic ...



- Aliphatic carboxylic acids have the carboxyl group attached with an open chain of carbon ... may be represented by the general formula

C_nH_{2n+1}-COOH Or  *where R=H or any alkyl group*

- There are organic compounds which contain more than one carboxylic groups in the same molecule. Thus dicarboxylic acids and tricarboxylic acids etc. are formed.

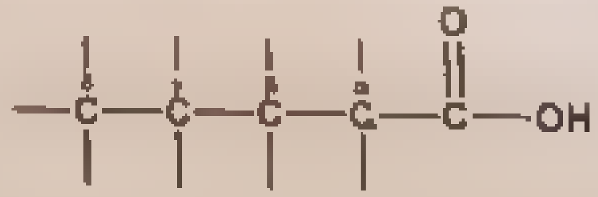
NOMENCLATURE

Common Names

(1) Many carboxylic acids are known by their common names.

(2) The positions of other groups attached with the chain containing the carboxyl group are indicated by Greek letters α, β etc.

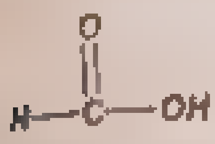
(3) The carbon adjacent to the carboxylic group is called the α (alpha) carbon. The carbon atom in the ... group is not the α carbon e.g.



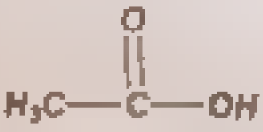
The IUPAC System

Aliphatic Carboxylic Acids

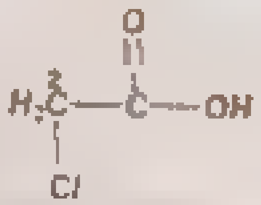
1. Select the longest carbon chain containing the carboxyl group.
2. Change the 'e' of the corresponding alkane to "oic acid".
3. Numbering of the carbon begins with the carbon of the carbonyl group.
4. Since the carboxyl group is always present at one end, therefore its position is not mentioned.
5. Substituents are also named and their position is indicated.



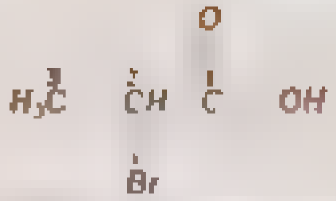
Methanoic acid



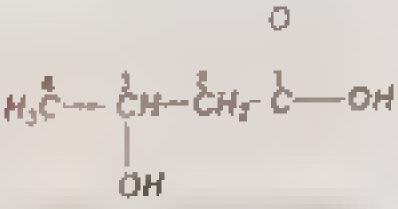
Eethanoic acid



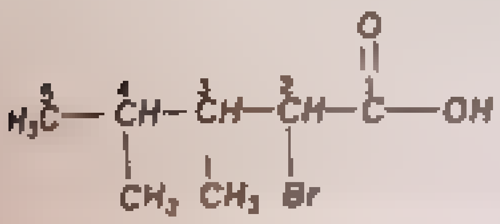
2 Chloroethanoic acid



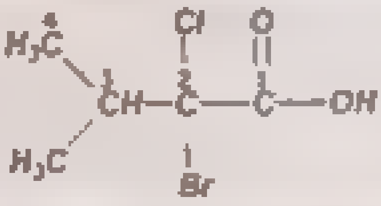
2 Bromopropanoic acid



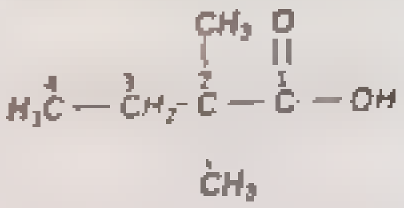
3 Hydroxybutanoic acid



2-Bromo-3,4-dimethylpentanoic acid

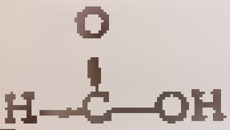


2 Bromo-2 chloro-3-methyl butanoic acid

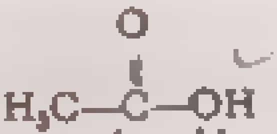


2,2-Dimethylbutanoic acid

The names and the structural formulas of [illegible] boiling points and melting points are also given.



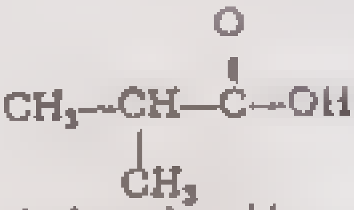
Formic acid
or
Methanoic acid
b.p., 101°C
m.p., 8·4°C



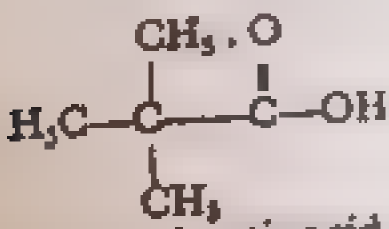
Acetic acid
or
Ethanoic acid
b.p., 118°C
m.p., 16°C,

Propionic acid
or
Propanoic acid
b.p., 142°C
m.p., −21°C

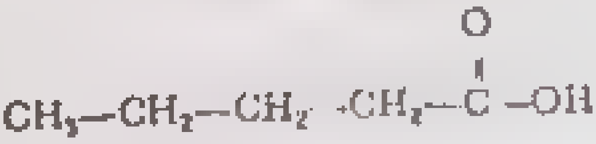
n-Butyric acid
or
Butanoic acid
b.p., 164°C
m.p., −5°C



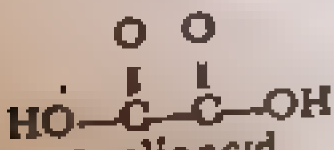
Isobutyric acid or
2—Methyl propanoic acid
b.p., 154°C
m.p., −47°C



Trimethylacetic acid
or
2,2—Dimethylpropanoic acid
b.p., 164°C
m.p., 35·5°C



n—Valeric acid
or
pentanoic acid
b.p., 186°C
m.p., −35°C

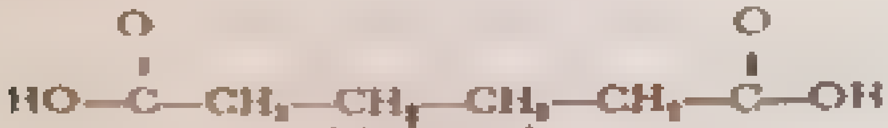


Oxalic acid
or
Ethanedioic acid
m.p., 186°C
(decomp.)

Malonic acid
or
Propanedioic acid
m.p., 130—135°C
(decomp.)

Succinic acid
or
Butanedioic acid
m.p., 182°C

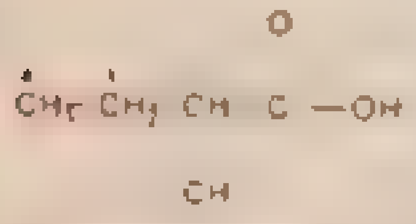
Glutaric acid
or
Pentanedioic acid
m.p., 97·7°C

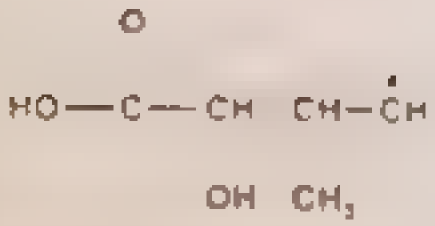


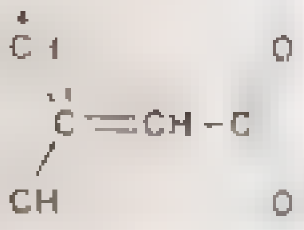
Adipic acid
or
Hexanedioic acid
m.p., 151—153°C

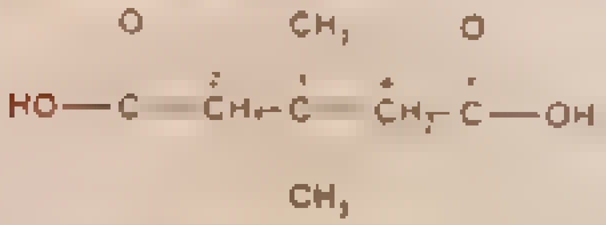
MORE PRACTICE

/CH CH CH(CH)COOH

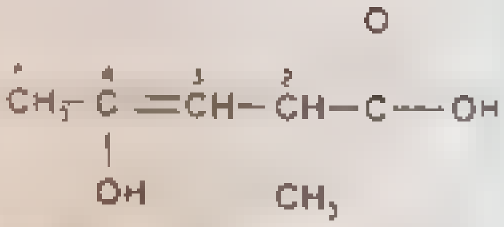




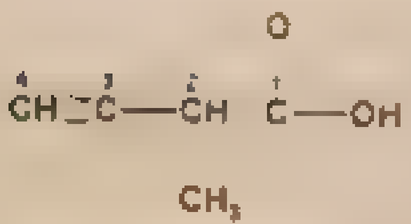




3,3-Dimethylpentanedioic acid

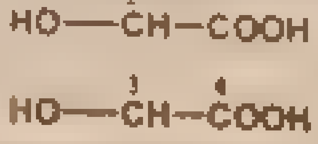


...ethyl 3-pentenoic acid

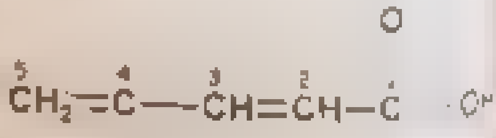


2-Methyl-3-butynoic acid

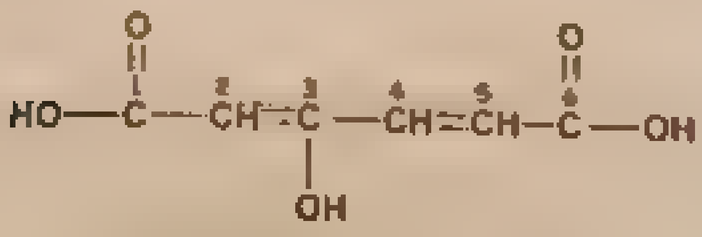
HOOC CH(OH) CH(OH) COOH



2,3-Dihydroxybutanedioic acid



4-Hydroxypenta-2,4-dienoic a...



3-Hydroxyhexadienedioic acid

PHYSICAL PROPERTIES:

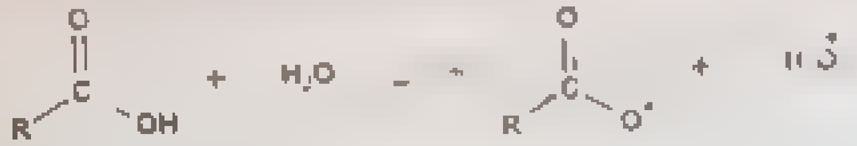
The C=O and O-H groups are polar due the electronegativity difference [illegible]
The polar nature of both the O–H and C=O bonds results in the formation [illegible] with other carboxylic acid molecules or other H-bonding systems (e.g. water).
The results are
- higher melting and boiling points compared to similar alcohols
- high solubility in aqueous media
- hydrogen bonded dimers in gas phase and dimers or aggregates in the liquid

STRUCTURE:

- The COOH unit is planar and consistent with sp^2 hybridization.
- There is a resonance interaction of the lone pairs of the hydroxyl oxygen with the p system of the carbonyl as shown in the figure

ACIDITY:

- Carboxylic acids are the most acidic simple organic compounds (pKa [illegible]) compare with alcohols (pKa~ 16). *Remember*: the lower the pKa, the stronger the acid. [illegible] donation of proton [illegible] stability of carboxylate anion. More ease of donation [illegible] anion, stronger the acid. However they are only weak acids compared [illegible]
- The carboxylate ion is stabilized due to resonance (eq. 2). The [illegible] negative charge takes place between two electronegative oxygen atoms.



2

- Adjacent [illegible] electron withdrawing substituents increase the acidity because they withdraw negative charge and thus further stabilize the carboxylate anion.

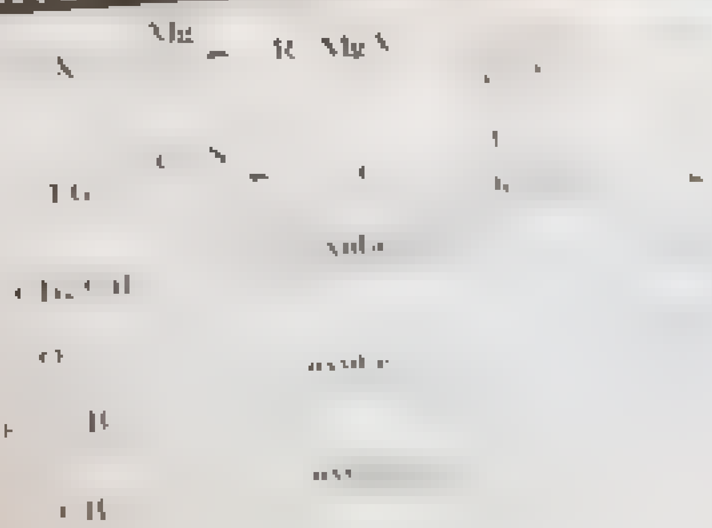
Carboxylic Acid	Structure	pKa
Ethanoic acid	CH_3CO_2H	4.7
Propanoic acid	$CH_3CH_2CO_2H$	4.9
Fluoroethanoic acid	CH_2FCO_2H	2.6
Chloroethanoic acid	CH_2ClCO_2H	2.[illegible]

Carboxylic Acid	Structure	pKa
[illegible]	[illegible]	1.3
Trichloroethanoic acid	[illegible]	[illegible]
Nitroethanoic acid	[illegible]	[illegible]

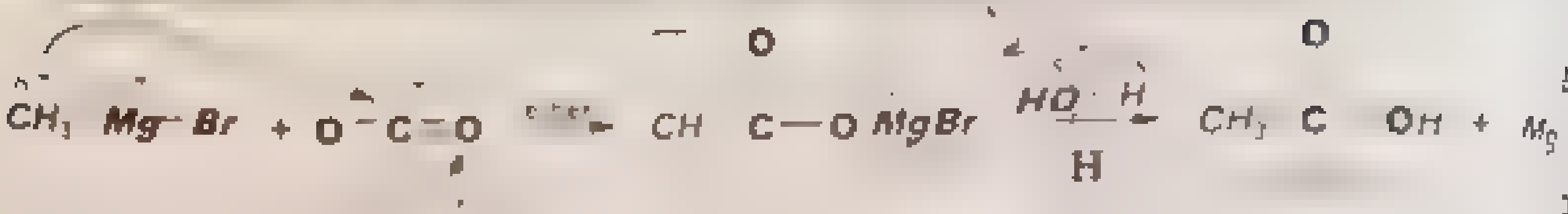
PREPARATIONS OF CARBOXYLIC ACIDS

Summary

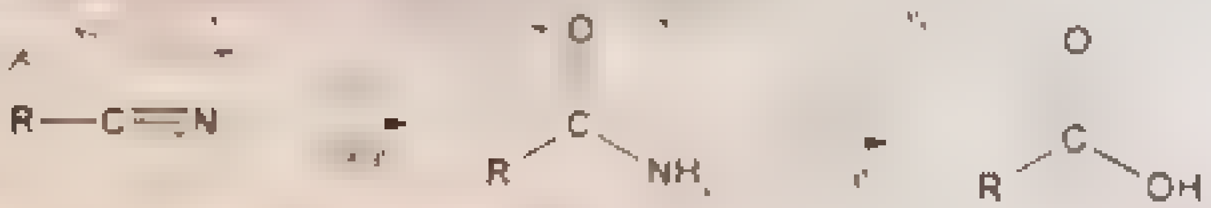
- Carbonation of Grignards
- Hydrolysis of Nitriles
- Oxidation of 1° Alcohols
- Oxidation of Aldehydes
- Oxidation of Alkyl Benzenes



(1) CARBONATION OF GRIGNARD REAGENTS, RMgX, BY CO_2



(2) HYDROLYSIS OF NITRILES



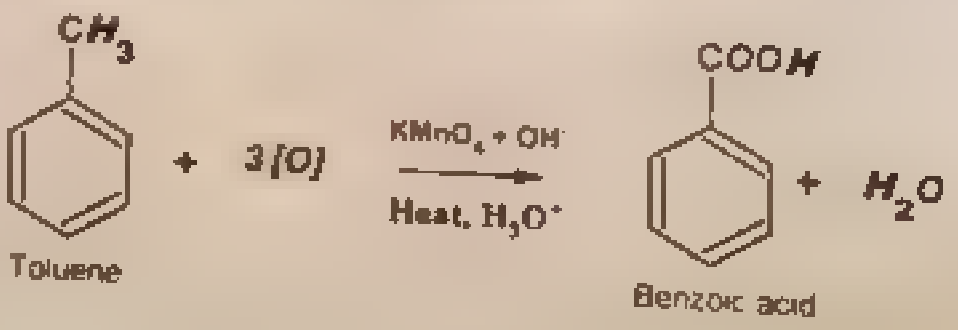
(3) OXIDATION OF PRIMARY ALCOHOLS

(4) OXIDATION OF ALDEHYDES

Aldehydes are oxidized ...

(5) OXIDATION OF ALKYL BENZENES

Alkyl side chain on aromatic ring is oxidized to carboxyl group



REACTIVITY

- The carboxyl group [illegible] CH_3 [illegible] groups
- In most reactions the carboxyl group [illegible]
- However [illegible] these [illegible] the presence [illegible]

REACTIONS OF CARBOXYLIC ACIDS

Carboxylic acids undergo the [illegible]

(A) The reaction in which [illegible] is involved (salt formation)

(B) The reaction in which OH group [illegible]

(C) The reaction [illegible]

(A) REACTION INVOLVING HYDROGEN ATOM OF THE CARBOXYL GROUP

Carboxylic acids [illegible] dissociate in water

$1° > 2° > 3°$ alcohol

$$R-\overset{O}{\overset{\|}{C}}-O-H \overset{H_2O}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-O^- + H^+$$

(Carboxylate ion)

In the presence of water [illegible] as H_3O^+ ion

(1) REACTIONS WITH BASES

Carboxylic acids react with base (NaOH, KOH) to form salts

$$CH_3-COOH + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3-COONa} + H_2O$$

(2) REACTION WITH CARBONATES AND BICARBONATES

Carboxylic acids decompose carbonate and [illegible] carbon dioxide gas with effervescence

$$2\,CH_3-COOH + Na_2CO_3 \longrightarrow \underset{\text{Sodium acetate}}{2\,CH_3-COONa} + H_2O + CO_2$$

$$CH_3-COOH + NaHCO_3 \longrightarrow \underset{\text{Sodium acetate}}{CH_3-COONa} + H_2O + CO_2$$

(3) REACTIONS WITH METALS

Carboxylic acids reaction with active metals like Na, K, Ca, Mg etc. to form their salts with the evolution of hydrogen gas

$$2\,CH_3-COOH + 2\,Na \longrightarrow \underset{\text{Sodium acetate}}{2\,CH_3-COONa} + H_2$$

(B) REACTION INVOLVING OH GROUP OF THE CARBOXYL GROUP

(1) PREPARATION OF ACYL CHLORIDES

- Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride [illegible]
- Acyl chlorides are by far the most common [illegible] of the acid halides

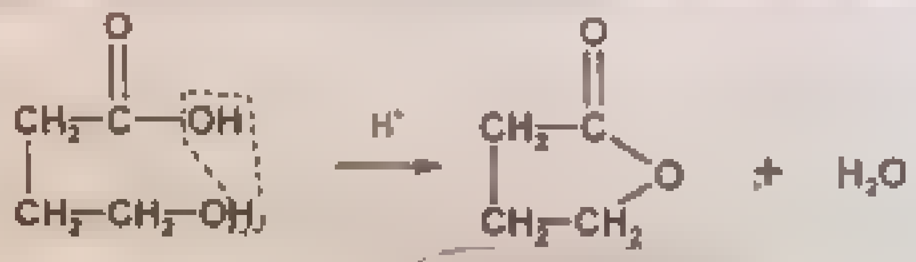
$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \xrightarrow{\text{pyridine}} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

(2) PREPARATION OF ACID ANHYDRIDES

(3) PREPARATION OF ESTERS

Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an ...

- This reaction is also known as the **Fischer esterification**
- The equilibrium can be driven to completion by using an excess of either the alcohol or the carbo... or by removing the water as it forms
- Alcohol reactivity order is $CH_3OH > 1° > 2° > 3°$. It is due to steric effects. Thus, larger ... lesser the reactivity
- Esters can also be made from other carboxylic acid derivatives ... reacting them with the appropriate alcohol in the presence of a weak base
- If a compound contains both hydroxyl and carboxyl ... lactones via an intramolecular reaction. Reactions that form 5 or 6 membered ...



(Lactone Cyclic Ester)

Mechanism for Reaction for Acid Catalyzed Esterification

Step 1:

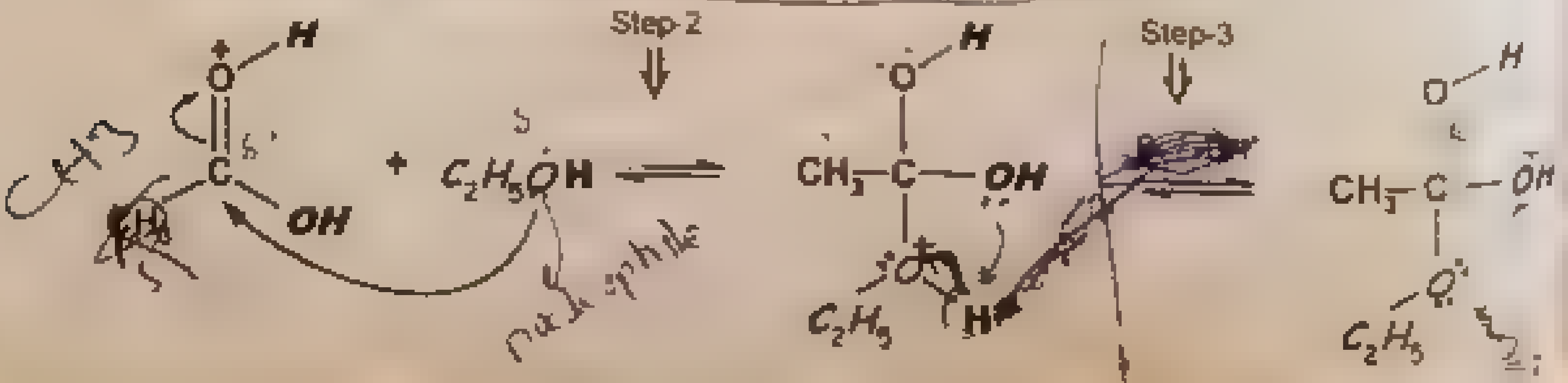
The O atom of carbonyl groups accepts a proton. The protonation of the carbonyl ... electrophilic. It is an acid/base reaction.

Step 2

The O-atom of alcohol functions as the nucleophile and attacks the electrophilic C ... are moved towards the oxonium ion and a tetrahedral intermediate is formed

Step 3

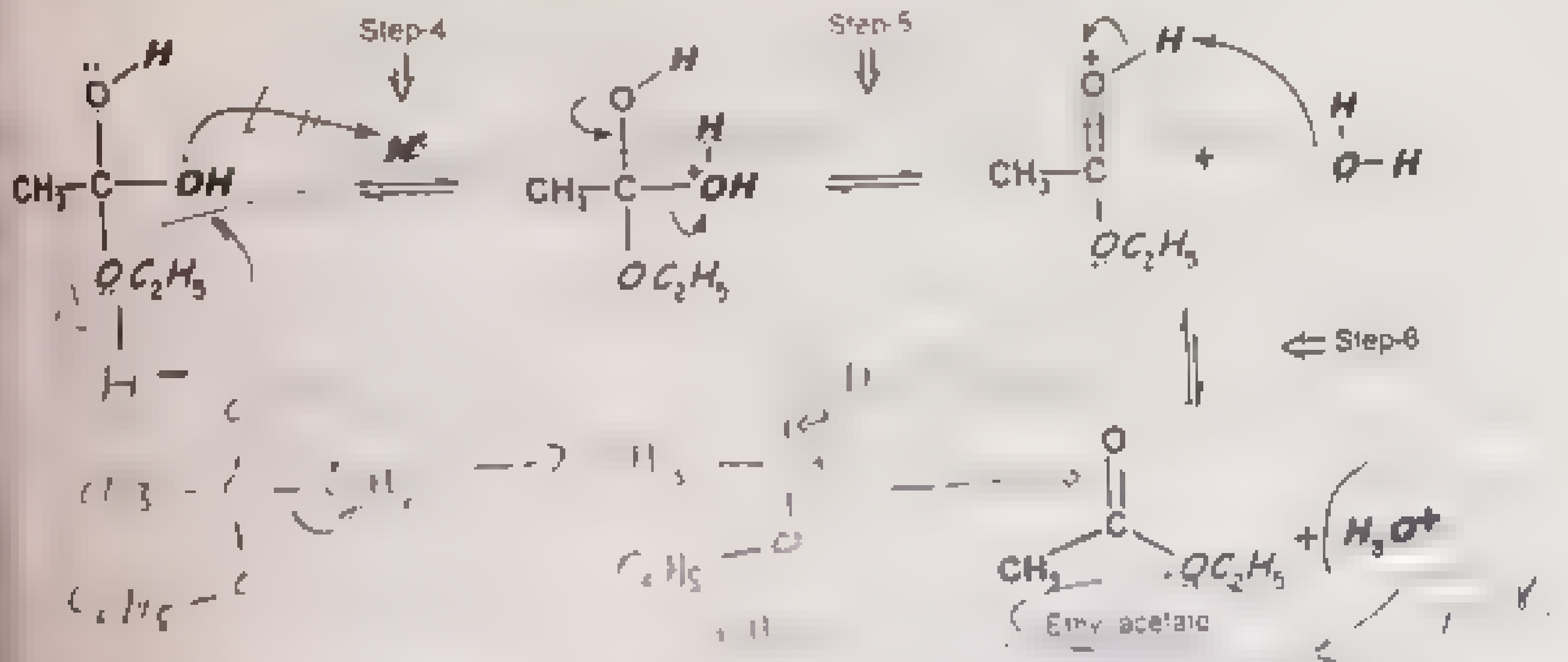
An acid/base reaction occurs. The alcoholic oxygen atom is deprotonated.



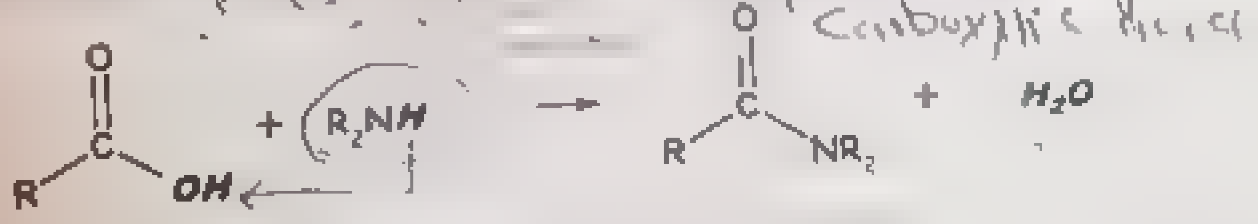
Step 4:
An acid/base reaction occurs. The -OH is to be removed. However, it is not a good leaving group, therefore it is converted it into a good leaving group by protonation.

Step 5:
The electrons of an adjacent oxygen help to push out the leaving group as a neutral water molecule and an oxonium ion is produced.

Step 6:
An acid/base reaction occurs. The oxonium ion is deprotonated to give the ester product.



(4) PREPARATION OF AMIDES



In general, it is not easy to prepare amides directly from the parent carboxylic acid. It is because, the acid will protonate the amine. Thus, further reaction is stopped since the carboxylate is a poor electrophile and the ammonium ion is not nucleophilic.

It is much easier to convert the carboxylic acid to the more reactive ...

(C) REACTION INVOLVING COOH GROUP AS A WHOLE

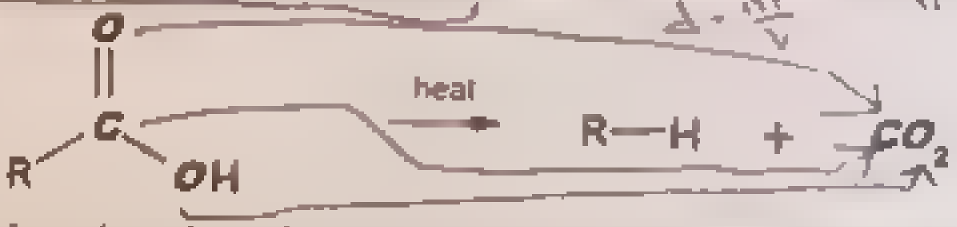
(1) REDUCTION TO ALCOHOLS

Carboxylic acids are reduced to **primary alcohols**

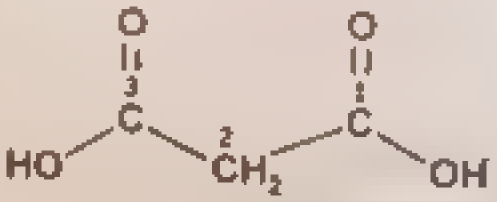
Carboxylic acids are less reactive to reduction [illegible] T[illegible] acids can only be reduced by $LiAlH_4$ and **NOT** by the less reactive [illegible]

(2) DECARBOXYLATION

Def. Loss of carbon dioxide is called **decarboxylation**



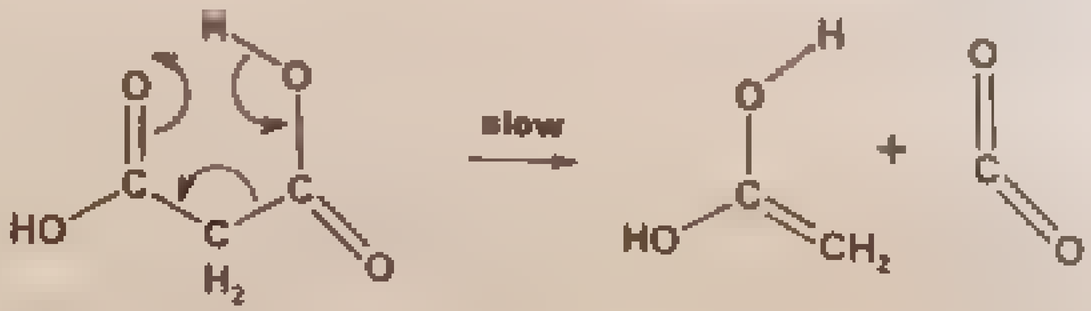
- Simple carboxylic acids rarely undergo decarboxylation
- Carboxylic acids with a carbonyl group at the 3 or 5 position readily undergo [illegible] e.g. derivatives of malonic acid



The reaction proceeds via a cyclic transition state giving an enol intermediate that tautomerizes [illegible]

Step 1.

The reaction mechanism involves transfer of the proton from the O-H group of one [illegible] of the other COOH group. Thus, O-H and C-C bonds are broken and π bonds are formed. The reaction [illegible] concerted nature

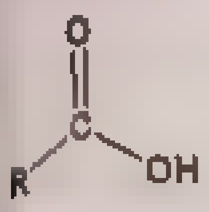


Step 2

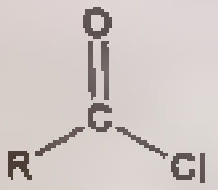
Tautomerization of the enol of the carboxylic acid forms the the acid product

ELABORATION OF REACTIONS THAT INTERCONVERT CARBOXYLIC ACIDS

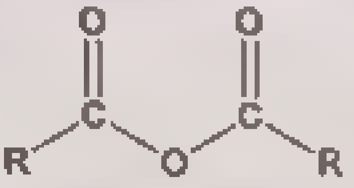
The carboxylic acid derivatives are a **family** of closely related functional groups



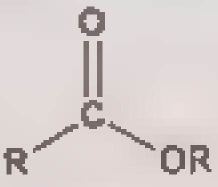
Carboxylic acid



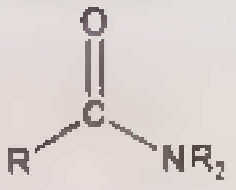
Acyl halide



Acid anhydride



Ester



Amide

- Each contain a C=O group with a **heteroatom** attached. Thus these are different from aldehydes and ketones
- They can all be prepared from the parent carboxylic acid. On hydrolysis they all convert back to the parent carboxylic acid
- They share a common reactivity pathway with nucleophiles called **Nucleophilic Acyl Substitution**

IMPORTANT
The reactivity order is acyl chloride > anhydride > ester = carboxylic acid > amide > carboxylate

REACTIONS OF CARBOXYLIC ACID DERIVATIVES

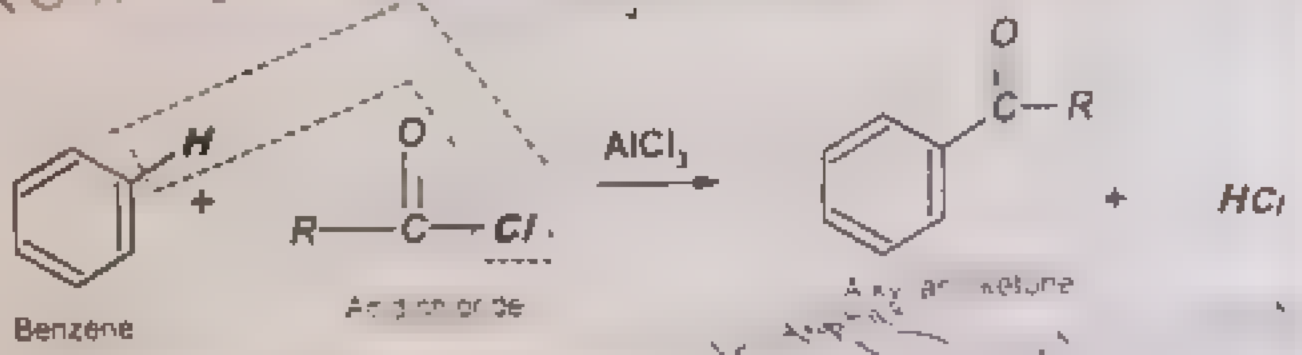
REACTIONS OF ACYL HALIDES

- Acyl chlorides are the most reactive of the carboxylic acid derivatives. Therefore can be readily converted into other carboxylic acid derivatives.
- They react quite readily with cold water and hydrolyze to the carboxylic acid. The HCl by-product is usually removed by adding a base such as pyridine or triethylamine.

acid anhydride

FRIEDEL-CRAFTS ACYLATION OF BENZENE

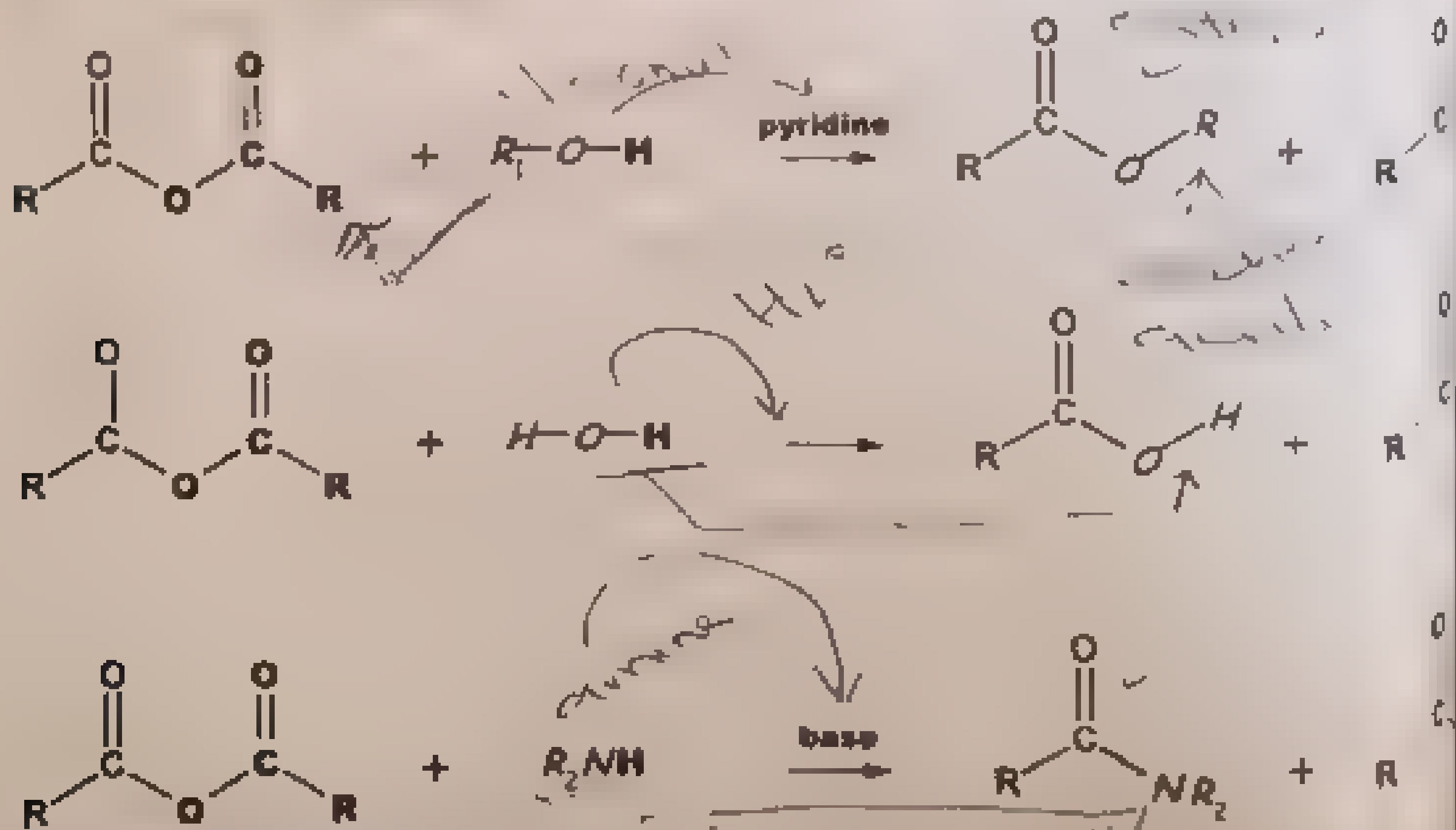
atom with c



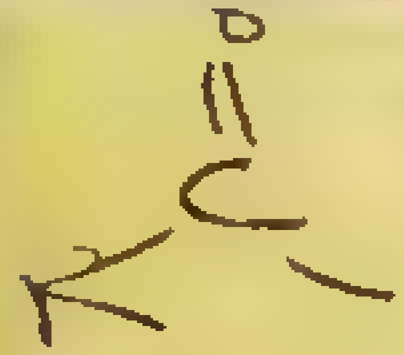
1 • Overall transformation: Ar-H to Ar-COR (a ketone)
2 • Named after Friedel and Crafts who discovered the reaction
3 • **Reagent**: normally the acyl halide (e.g. usually RCOCl) with aluminum trichloride catalyst.
zone rich in electron
4 • The $AlCl_3$ enhances the electrophilicity of the acyl halide by complexing with the halide
5 • ***Electrophilic species***: the acyl cation or **acylium ion** i.e. RCO^+ formed by the reaction of the acyl halide with the Lewis acid catalyst
6 • Friedel-Crafts reactions are limited to arenes as or more reactive than mono halobenzenes.
7 • Other sources of acylium can also be used such as acid anhydrides with $AlCl_3$
9 • The reaction can still be called as a ***Nucleophilic Acyl Substitution*** of the acyl halide. It is because overall we have a nucleophile (here the p bond of an aromatic ring) replacing the leaving group (chloride) at the electrophilic C=O

REACTIONS OF ACID ANHYDRIDES

- Acid anhydrides are the second most reactive of the carboxylic acid derivatives and can be readily converted into the other less reactive carboxylic acid derivatives (see above)
- A base in often added to neutralize the carboxylic acid by product that is formed



Lewis base
Lone pair donor
NH_3, H_2O
Nucleophiles CH_3S^-
Lewis acid
• Lone pairs accept BF_3, Al
• electrophile Al^{3+}, Fe^{3+}
• The proton

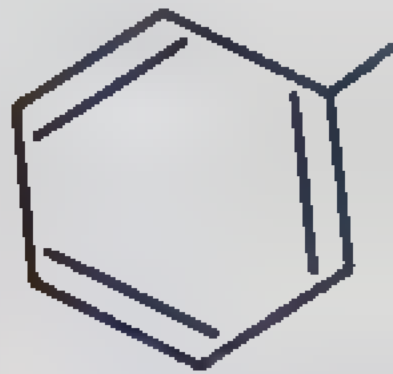


* An acyl group is a functional group with formula RCO - where R is bound to the carbon atom with a single bond

- Acyl groups are formed when one or more hydroxyl groups (-OH) are removed from an oxoacid.

Ester, ketones, ald, amides — acid contains oxygen atom bonded to a hydrogen atom, with other ...

a functi...
where
...ound
bond.



Alkyl an...

-lectrophile

REACTIONS OF ESTERS

Esters can be converted into other esters (transesterification) ...

TRANSESTERIFICATION

Heat the ester with alcohol and acid catalyst ...

HYDROLYSIS

Heat the ester with aq. acid or base (e.g. aq. H_2SO_4 or aq. NaOH) ...

AMIDE PREPARATION

Heat the ester with the amine (methyl or ethyl esters are the most reactive)

HYDROLYSIS OF ESTERS

Carboxylic esters hydrolyze to the parent carboxylic acid and an alcohol.

Reagents: aqueous acid (e.g. H_2SO_4) / heat, or aqueous NaOH / heat (known as *saponification*)

carboxylic ester

Reaction under BASIC conditions.

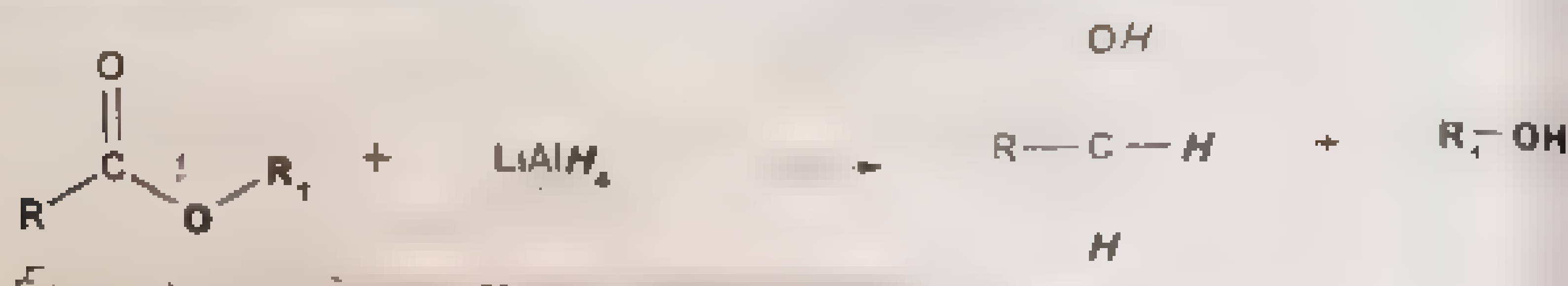
- The mechanism shown leads to acyl-oxygen cleavage
- The mechanism is supported by experiments using ^{18}O labeled compounds ...
- This reaction is known as "**saponification**" because it is the basis of making soap from glycerol triesters (fats).
- The mechanism is an example of the reactive system type

Reaction under ACIDIC conditions.

- The acid catalyzed mechanism is the reverse of the Fischer esterification
- The mechanism shown also leads to acyl-oxygen cleavage
- The mechanism is an example of the less reactive system type

REDUCTION OF ESTERS

Carboxylic esters are reduced ... the reaction ... the carboxylic ...



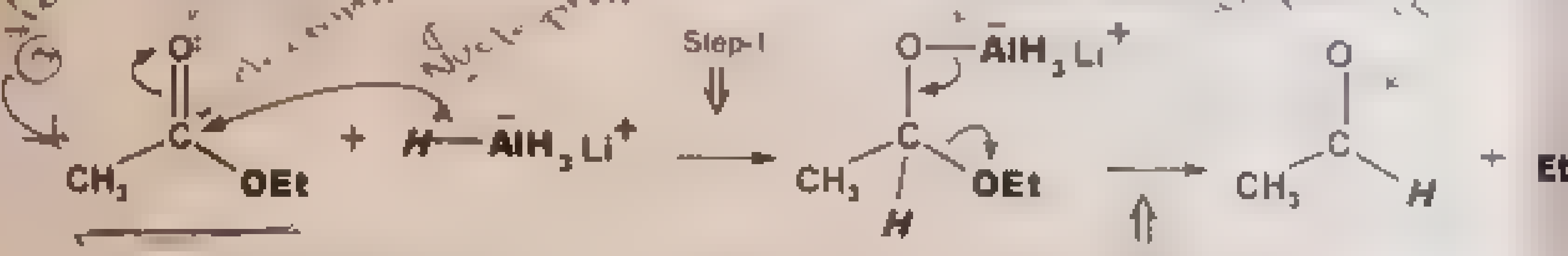
- Esters are less reactive towards Nu ...
- They can only be reduced ... NOT ...
- The reaction requires that 2 h...
- The mechanism is an example of the ...
- Note the aldehyde intermediate

Step 1:

- The nucleophilic H from the hydride ... the ester
- The electrons from the C=O move to the electronegative ... alkoxide complex

Step 2

- The tetrahedral intermediate collapses and displaces the ...
- This produces an aldehyde as an intermediate



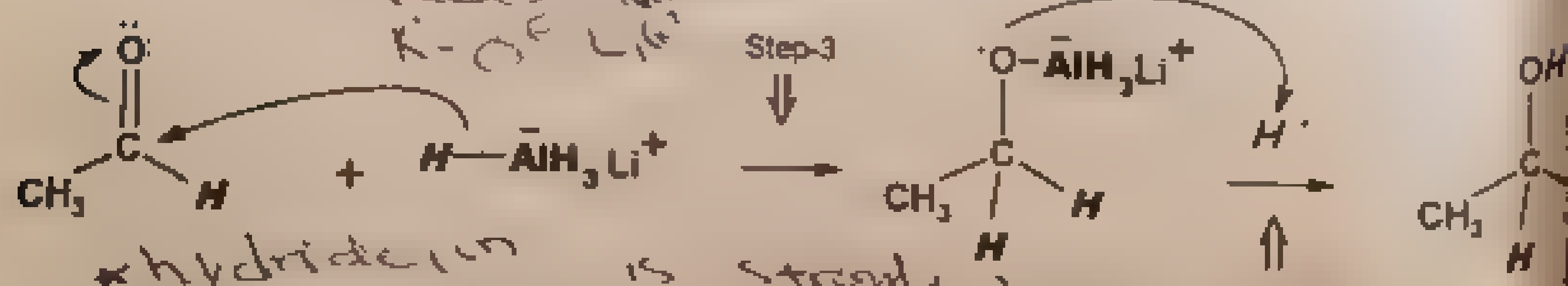
Step 3.

- Now the aldehyde is reduced. The nucleophilic H from the hydride reagent adds to the electrophilic C of the polar carbonyl group of the aldehyde.
- The electrons from the C=O move to the electronegative O creating an intermediate ... alkoxide complex

Step 4

- This is the work-up step. It is a simple acid base reaction.
- Protonation of the alkoxide oxygen produces the primary alcohol product from the intermediate complex

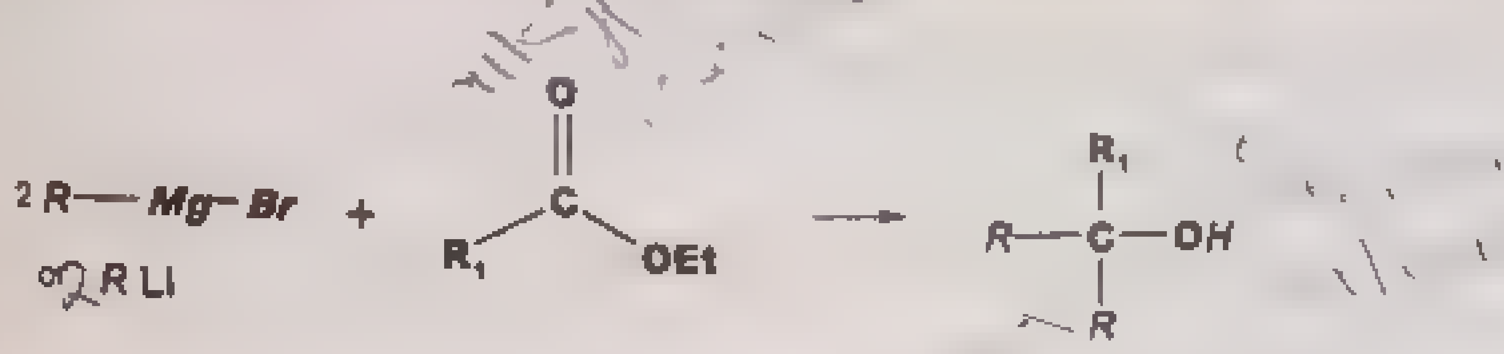
conjugate base of alcohol



* hydride ion is strong base but not nucleophilic. A reagent that acts as the hydride ion would if it were nucleophilic called a hydride reagent

REACTIONS OF RLi AND RMgX WITH ESTERS

Carboxylic esters, R'CO$_2$R", react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.



- The tertiary alcohol that results contains 2 identical alkyl groups (from R in the scheme)
- The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent (review)
- Since the ketone is more reactive than the ester the reaction cannot be used as a preparation of ketones
- The mechanism is an example of the reactive system type

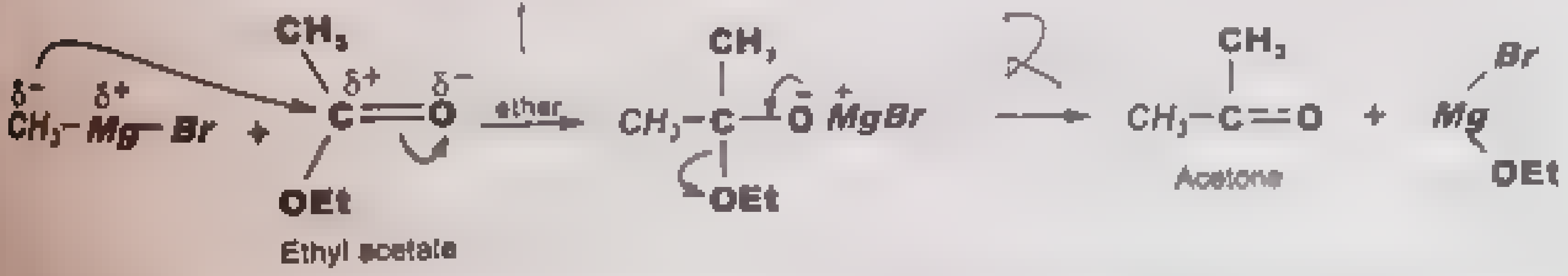
Mechanism

Step 1:

- The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester.
- The electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

Step 2:

- The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group
- This produces a ketone as an intermediate

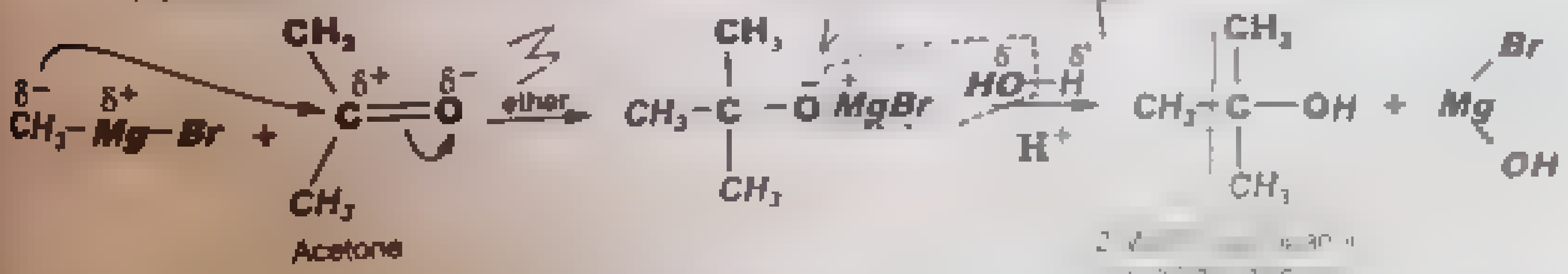


Step 3:

- The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone
- The electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

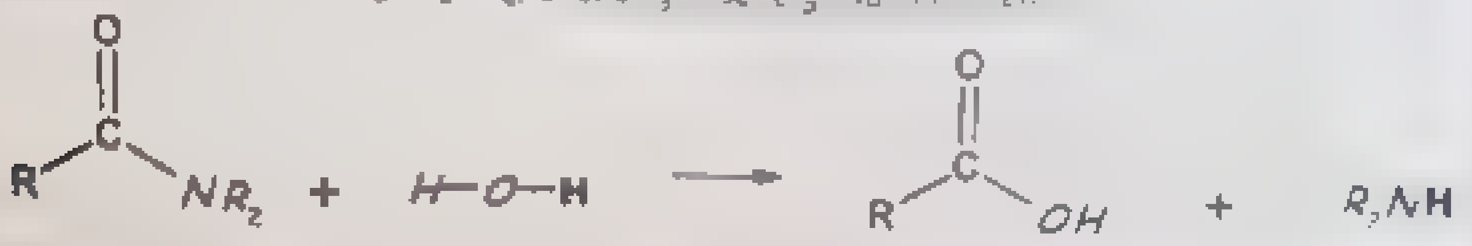
Step 4.

- This is the work-up step. It is a simple acid base reaction.
- Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex



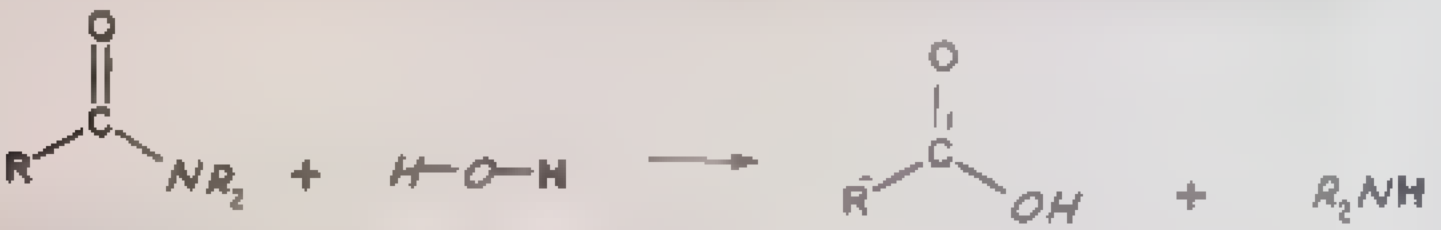
REACTIONS OF AMIDES

- Amides are the least reactive of the neutral carboxylic acid derivatives.
- The only interconversion reaction that amides undergo is hydrolysis back to the parent carboxylic acid and the amine
- Reagents: Strong acid (e.g. H_2SO_4) or strong base (e.g. NaOH), heat



HYDROLYSIS OF AMIDES

- Amides hydrolyze to the parent carboxylic acid and the appropriate amine
- The mechanisms are similar to those of esters
- Reagents: Strong acid (e.g. H_2SO_4), heat (preferred) or strong base (e.g. NaOH), heat



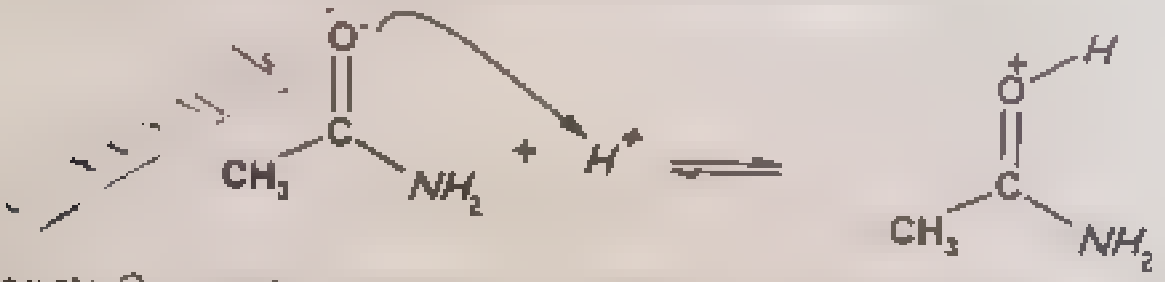
REACTION UNDER ACIDIC CONDITIONS

- Note that the acid catalyzed mechanism is analogous to the acid catalyzed hydrolysis of esters
- The mechanism shown below proceeds via protonation of the carbonyl not the amide N (see step 1)
- The mechanism is an example of the less reactive system type

MECHANISM OF THE ACID CATALYZED HYDROLYSIS OF AMIDES

Step 1:

- It is an acid/base reaction
- In this reaction water is a weak nucleophile and carbonyl group of amide is a weak electrophile so the ester is first activated by protonation
- Protonation of the amide carbonyl makes it more electrophilic

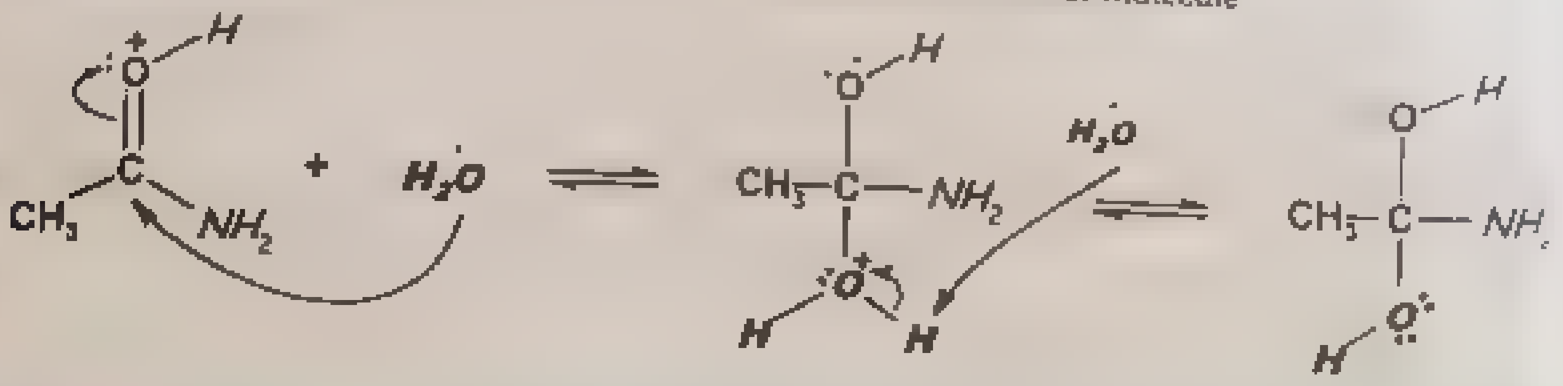


Step 2:

- The water O acts as the nucleophile and attacks the electrophilic C in the C=O
- The electrons are moved towards the oxonium ion, creating the tetrahedral intermediate

Step 3:

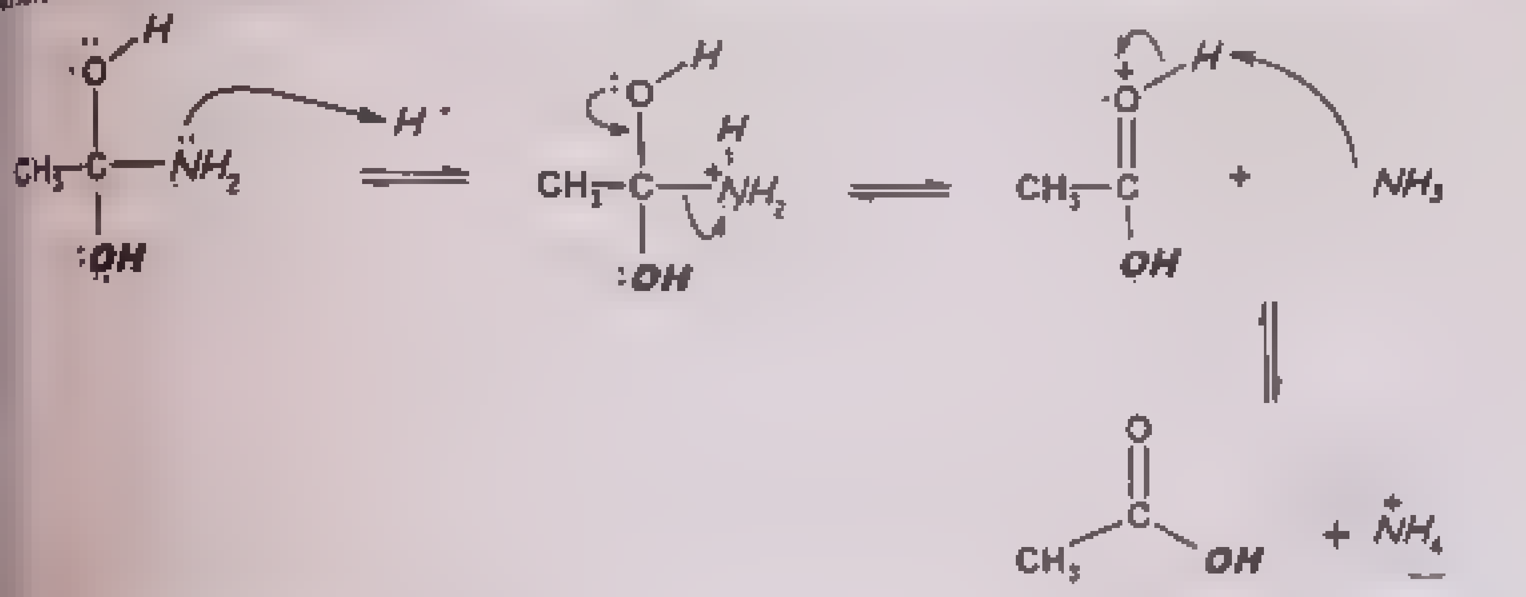
An acid/base reaction. Deprotonate the oxygen that came from the water molecule



Step 4:
It is an acid/base reaction. The $-NH_2$ group is to be removed. However it is a poor leaving group. So, it is converted into a good leaving group by protonation.

Step 5:
The electrons of adjacent oxygen are used to help "push out" the leaving group as a neutral ammonia molecule. Thus, oxonium ion is produced.

Step 6:
It is an acid/base reaction. Deprotonation of the oxonium ion forms the carboxylic acid product and regenerates the acid catalyst.



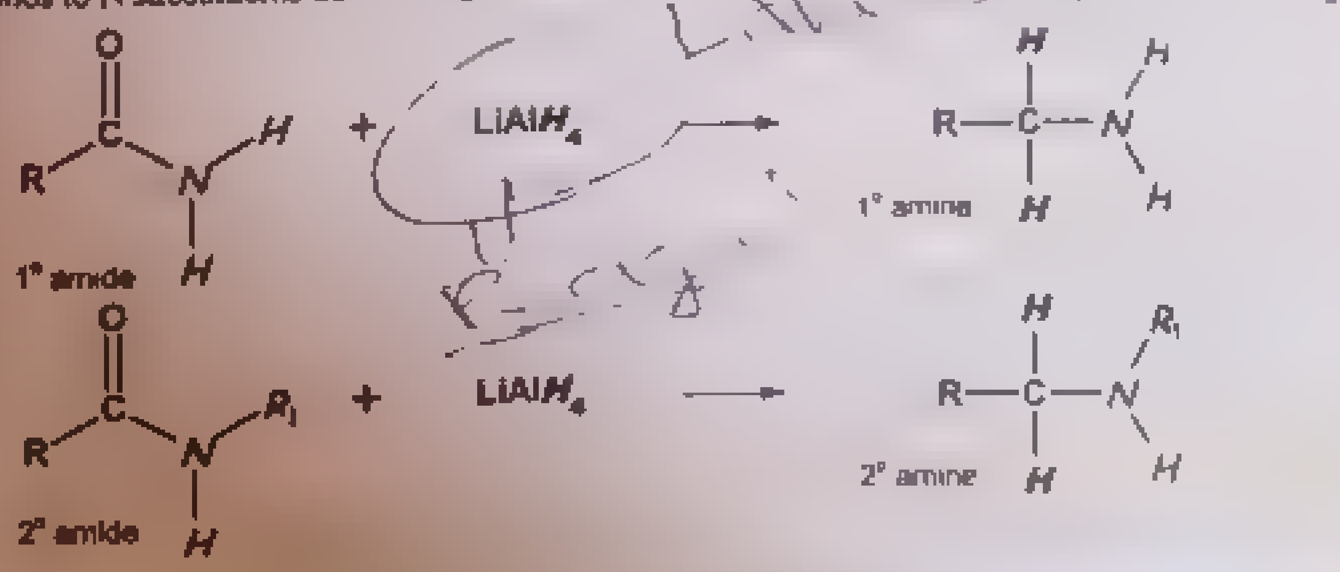
Acetic acid

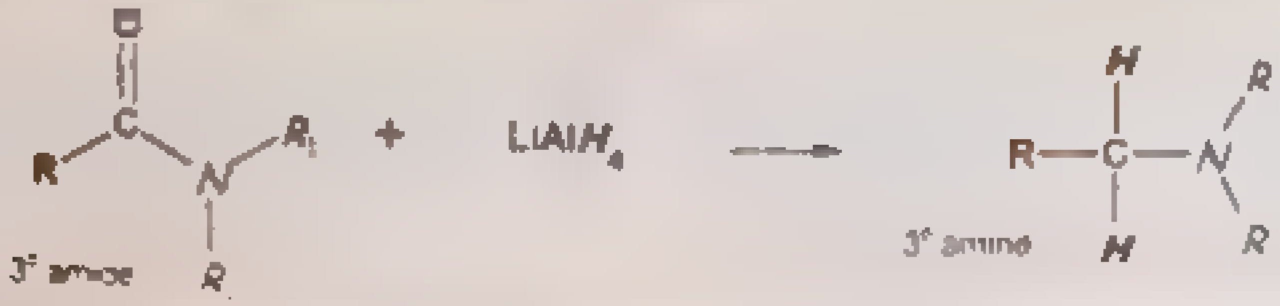
REDUCTION OF AMIDES

- Amides, $RCONR'_2$, can be reduced to the amine $RCH_2NR'_2$ by conversion of the C=O to $-CH_2-$
- Amides can be reduced by $LiAlH_4$ but NOT by the less reactive $NaBH_4$

Typical reagents: $LiAlH_4$ / ether solvent followed by aqueous work-up

- This reaction is different to that of other C=O compounds which reduce to ***alcohols***
- The nature of the amine obtained depends on the substituents present on the original amide
- The bonds to N substituents don't change





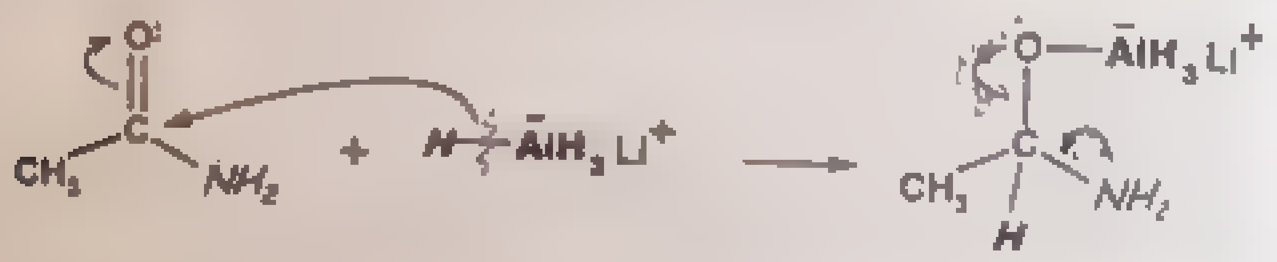
- R, R_1 or R_2 may be either alkyl or aryl substituents
- In the potential mechanism note that it is an O system that leaves. This is because [illegible] better leaving groups than the less electronegative N systems

Exercise Q3 (iii) *How amides are reduced with $LiAlH_4$? Give mechanism*

MECHANISM: REDUCTION OF AMIDE WITH $LiAlH_4$

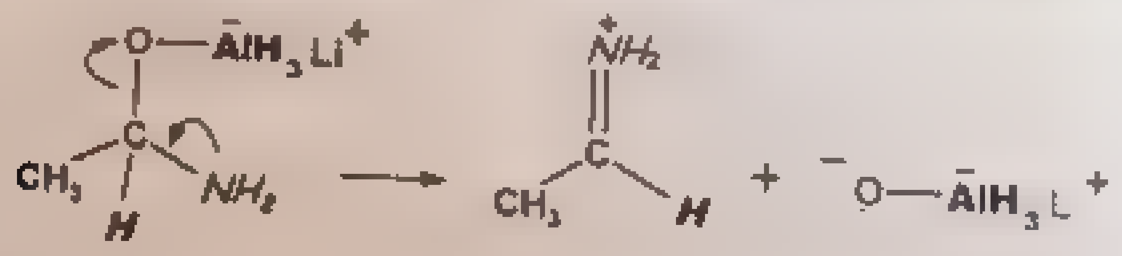
Step 1

- The nucleophilic H from the hydride reagent adds to the electrophilic C [illegible] the amide
- The electrons from the C=O move to the electronegative O creating an [illegible] complex



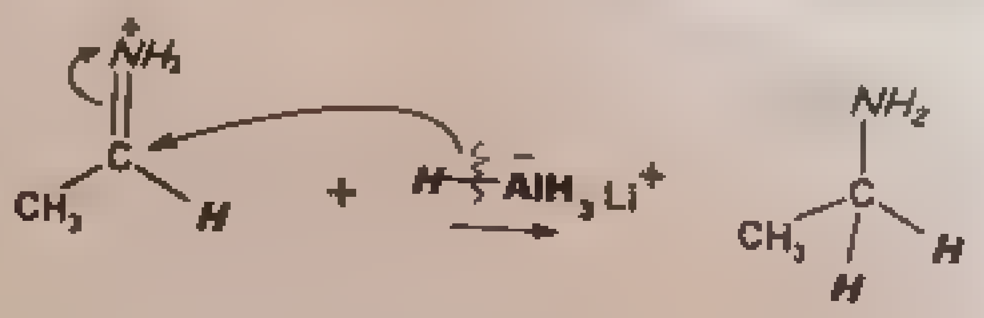
Step 2:

- The tetrahedral intermediate collapses and displaces the O as part of a metal alkoxide [illegible]
- This produces a highly reactive iminium ion an intermediate



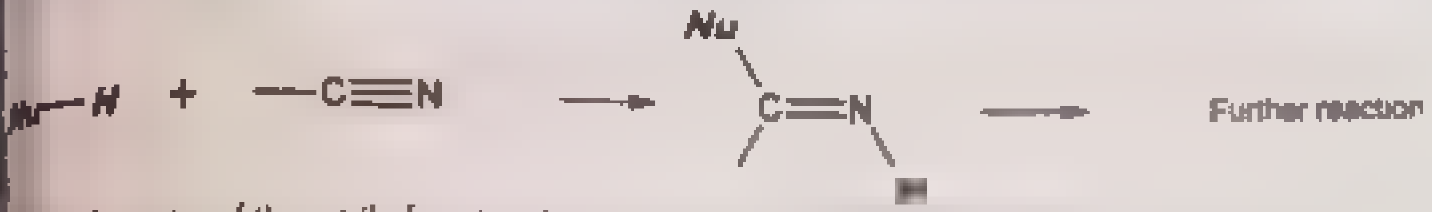
Step 3:

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the iminium system
- The π-electrons from the C=N move to the cationic N to neutralize the charge. Thus amine is p[illegible]

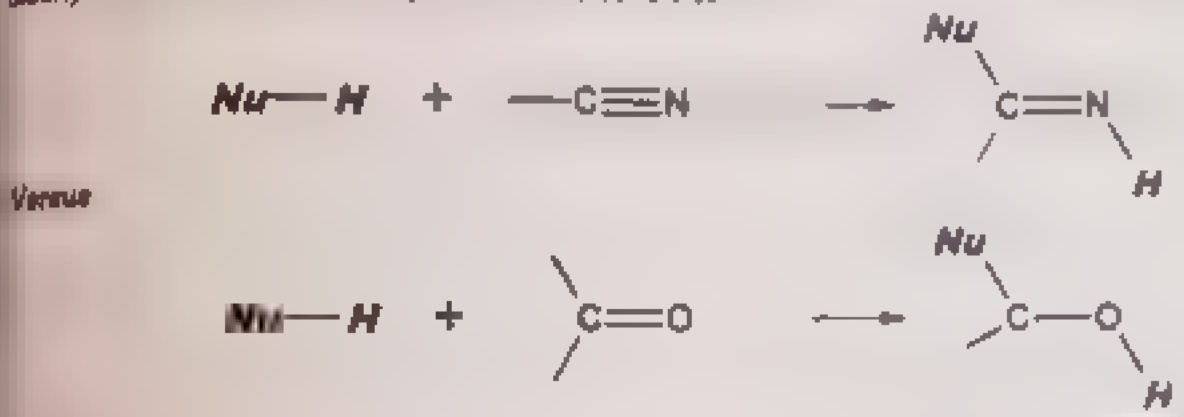


CTIONS OF NITRILES

Nitriles typically undergo nucleophilic addition to give products that often undergo a further reaction



The chemistry of the nitrile functional group, C≡N is very similar to that of the carbonyl, C=O of aldehydes and ketones. Compare the two schemes



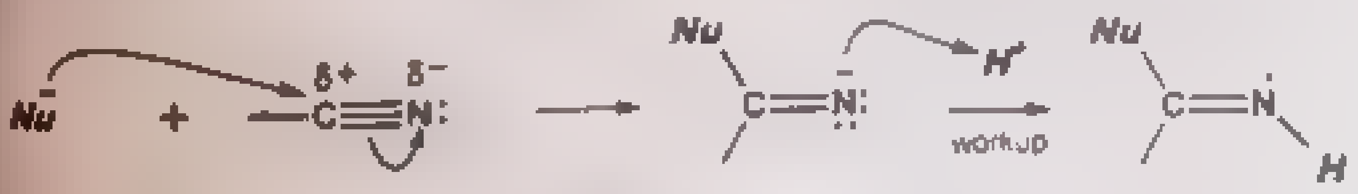
However, it is convenient to describe nitriles as carboxylic acid derivatives because

✓ the oxidation state of the C is the same as that of the carboxylic acid derivatives

✓ hydrolysis produces the carboxylic acid

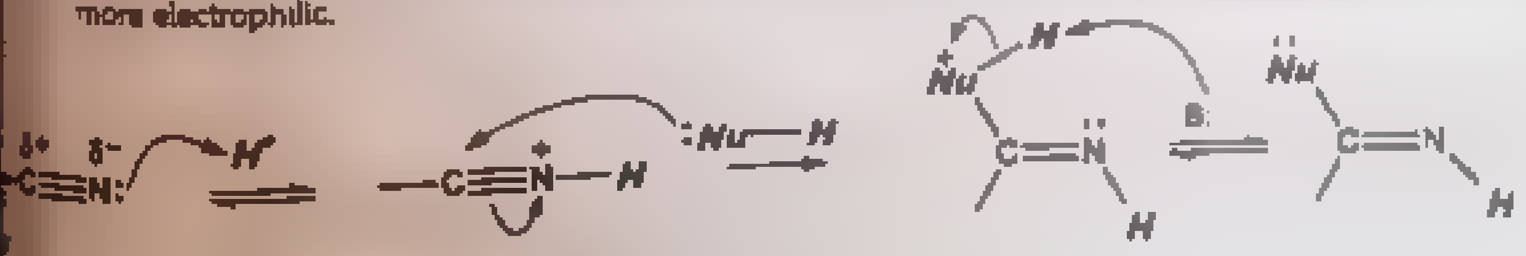
Like the carbonyl containing compounds, nitriles react with nucleophiles in two ways

(1) Strong nucleophiles (anionic) add directly to the **C≡N** to form an intermediate imine salt that protonates (and often reacts further) on work-up with dilute acid



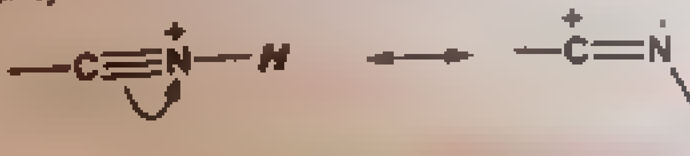
Examples of such nucleophilic systems are **RMgX, RLi, RC≡CM, $LiAlH_4$**

(2) Weaker nucleophiles (neutral) require that the **C≡N** be activated prior to attack of the **Nu**. This can be done using a acid catalyst which protonates on the Lewis basic N and makes the system more electrophilic.



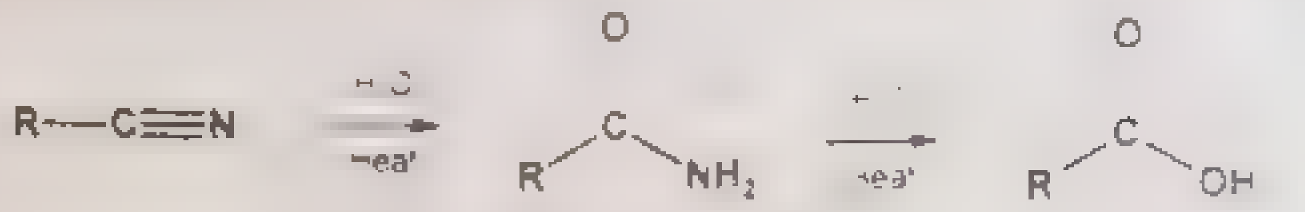
Examples of such nucleophilic systems are **H_2O, ROH**

The protonation of a nitrile gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.



HYDROLYSIS OF NITRILES

Nitriles RC≡N can be hydrolyzed to carboxylic acids RCO_2H via the amide $RCONH_2$



Reaction type: Nucleophilic Addition then Nucleophilic Acyl Substitution

Reagents: Strong acid (e.g. H_2SO_4) or strong base (e.g. NaOH)

Exercise Q2 (iv) *Give the mechanism for the acid catalyzed hydrolysis of a nitrile?*

MECHANISM ACID CATALYZED HYDROLYSIS OF NITRILES

Step 1:

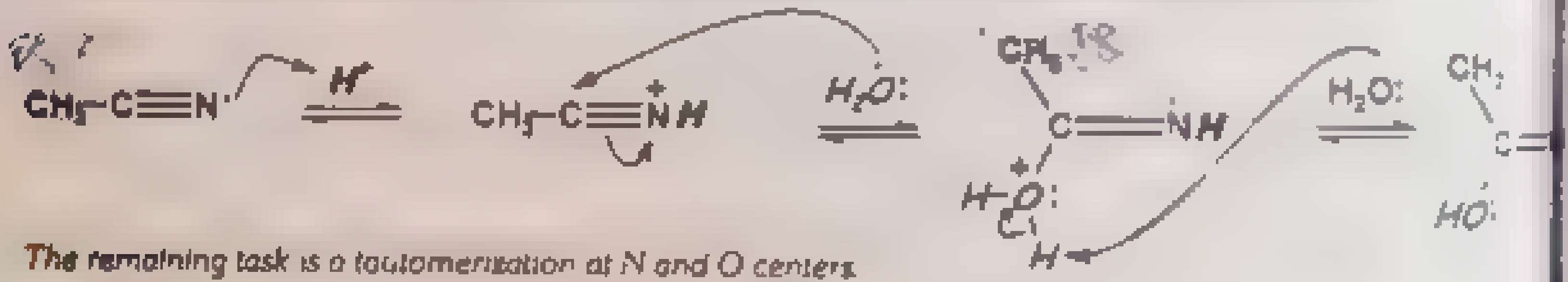
It is an acid base reaction. Since water is a weak nucleophile, therefore the nitrile is activated by protonation. So, the nitrile becomes more electrophilic

Step 2

- The water O acts as the nucleophile and attacks the electrophilic C in the C≡N
- The electrons are moved towards the positive center

Step 3:

It is an acid/base reaction. The oxygen that came from the water molecule is deprotonated



The remaining task is a tautomerization at N and O centers.

Step 4:

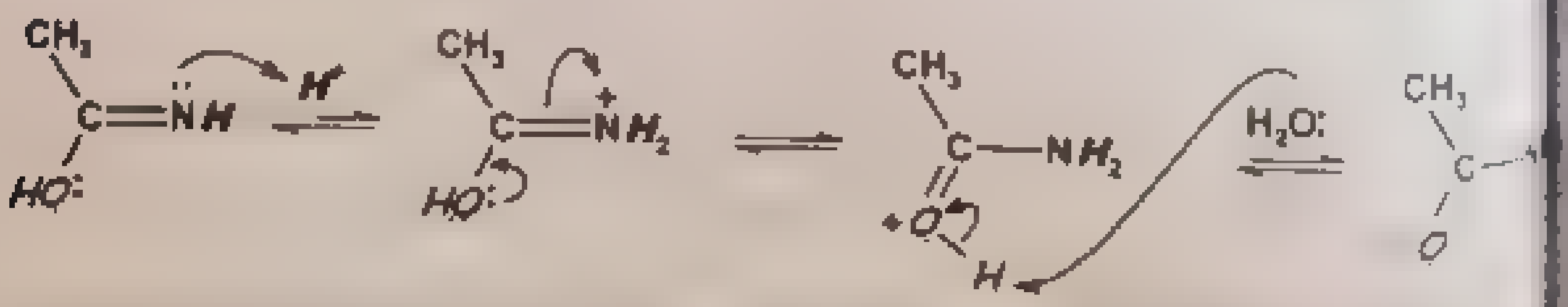
It is an acid/base reaction. The N atom is protonated to give the NH_2 group

Step 5:

The electrons of an adjacent O are used to neutralise the positive charge at the N atom and formed in the C=O. Thus an oxonium is produced.

Step 6:

It is an acid/base reaction. The deprotonation of oxonium ion produces the amide intermediate



The amide intermediate is half-way to the formation of acid. The hydrolysis of amide occurs in the same way described above in the "hydrolysis of amides"

REDUCTION OF NITRILES

- The nitrile, $RC \equiv N$ gives the 1° amine by conversion of the $C \equiv N$ to $-CH_2-NH_2$

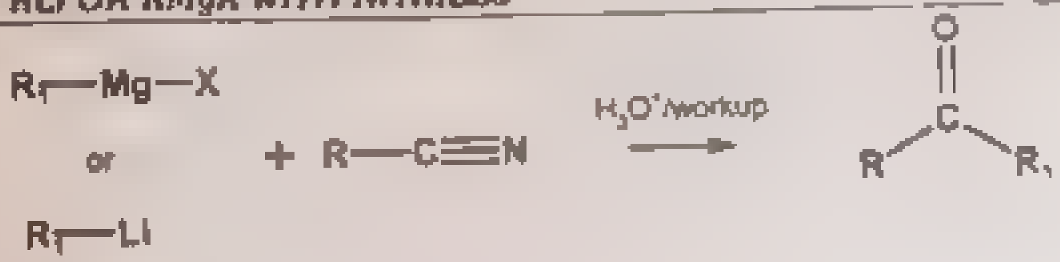
$$R-C\equiv N \xrightarrow{\text{Reduction}} R-CH_2-NH_2$$

- Reactions usually in Et_2O or THF followed by H_3O^+ work-up

Reaction type: *Nucleophilic Addition*

- Nitriles can be reduced by $LiAlH_4$ but **NOT** the less reactive $NaBH_4$
- Typical reagents: $LiAlH_4$ ether solvent followed by aqueous work up
- Catalytic hydrogenation (H_2 catalyst) can also be used giving the same products
- R may be either alkyl or aryl substituents

REACTIONS OF RLi OR RMgX WITH NITRILES



Reaction usually occurs in Et_2O (Diethyl ether) or THF

Reaction type: *Nucleophilic Acyl Substitution then Nucleophilic Addition*

- Nitriles, $RC \equiv N$, react with Grignard reagents or organolithium reagents to give ketones
- The strongly nucleophilic organometallic reagents add to the $C \equiv N$ bond in a similar fashion to that seen for <u>aldehydes and ketones</u>
- The reaction proceeds via an imine salt intermediate that is then hydrolyzed to give the ketone product

- Since the ketone is not formed until *after* the addition of water the orga[illegible] the opportunity to react with the ketone product
- Nitriles are less reactive than aldehydes and ketones

MECHANISM: REACTION OF RMgX WITH AN NITRILE

Step 1:

- The nucleophilic C in the organometallic reagent adds to the ele[illegible] C in the polar nitrile group
- The electrons from the $C \equiv N$ move to the electronegative N [illegible] complex

Step 2:

- It is an acid/base reaction
- On addition of aqueous acid the intermediate salt protonates giving the imine

Step 3:

- It is an acid/base reaction
- The imine is first activated by protonation acid catalysis

Step 4:

- The nucleophilic O of a water molecule attacks the electrophilic C ...
- The π electrons from the C=N move to the cationic N to neutralize the charge

Step 5

- It is an acid/base reaction
- The O atom from the water molecule is deprotonated to neutralize the positive charge

Step 6.

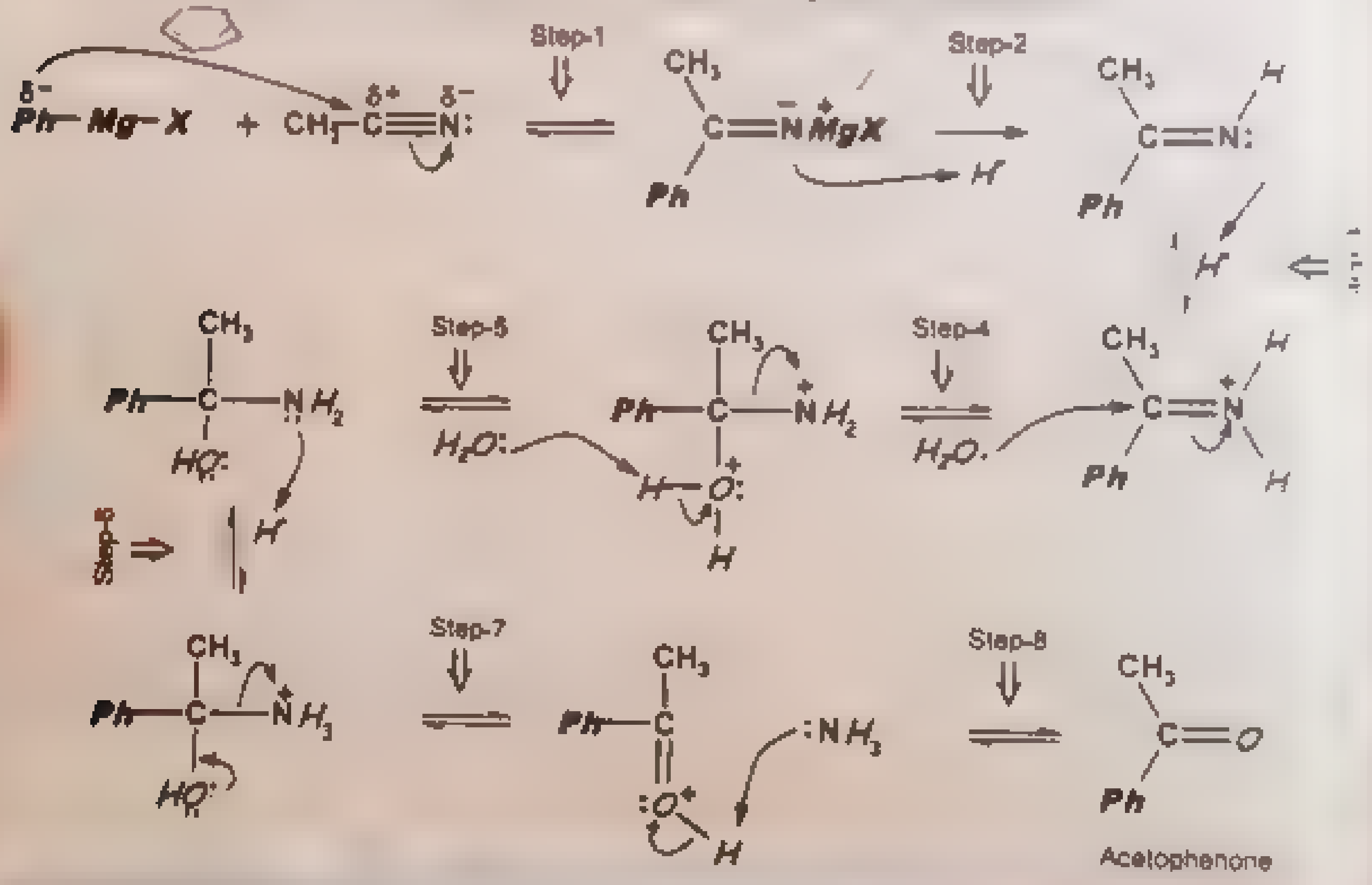
It is an acid/base reaction. The N system is converted into a better leaving group by protonation.

Step 7:

The electrons on the adjacent O are used to push out the N leaving group as a neutral molecule of ammonia. An oxonium ion is produced

Step 8.

It is an acid/base reaction. The deprotonation of oxonium ion gives the ketone product

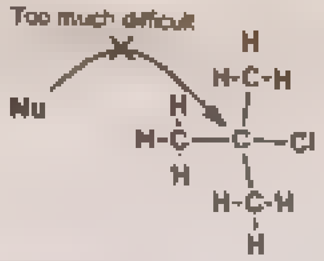


QUICK QUIZ

(1) Define Steric effect?

The effect of the three-dimensional configuration of reacting substances on the rate, nature, and extent of reaction is called steric effect.

e.g. The steric effect of three methyl groups in ter-butyl chloride causes hindrance to the approach of nucleophile on tertiary carbon. Therefore, tertiary butyl chloride does not give S_N2 reaction. Instead it gives S_N1 reaction. This hindrance is called steric hindrance



(2) What is alcohol's reactivity order?

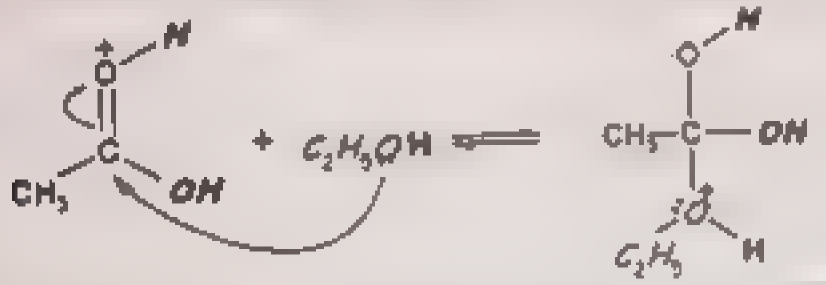
- Alcohol reacts with other reagents due to the breaking of C-O and O-H bonds
- If a nucleophile attacks, the C-O bonds breaks The order of reactivity of alcohols with respect to cleavage of C-O bond is

  Tertiary alcohol > Secondary alcohol > Primary alcohol
- If an electrophile attacks the O-H bond breaks. The order of reactivity of alcohol with respect to O-H bonds cleavage

  CH_3OH > Tertiary alcohol > Secondary alcohol > Primary alcohol

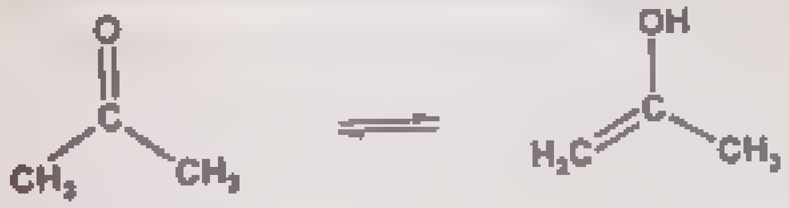
(3) How oxonium ion creates the tetrahedral intermediate

- The O-atom of alcohol functions as the nucleophile and attacks the electrophilic C in protonated carbonyl compound.
- The electrons are moved towards the oxonium ion and a tetrahedral intermediate is formed



(4) Define tautomerization?

The process of conversion of one tautomer into the other is called tautomerization



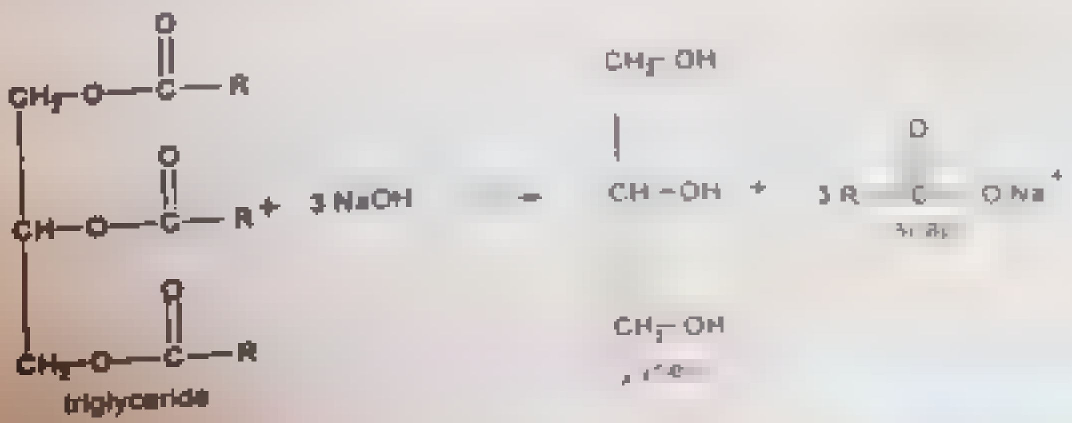
Keto tautomer Enol tautomer

(5) Define saponification?

The hydrolysis of fats with alkalies to produce soap is called saponification reaction

In this reaction sodium or potassium salt of fatty acids are produced. These salts are called soaps

Glycerol is also produced as a by-product



DO YOU KNOW?

1)

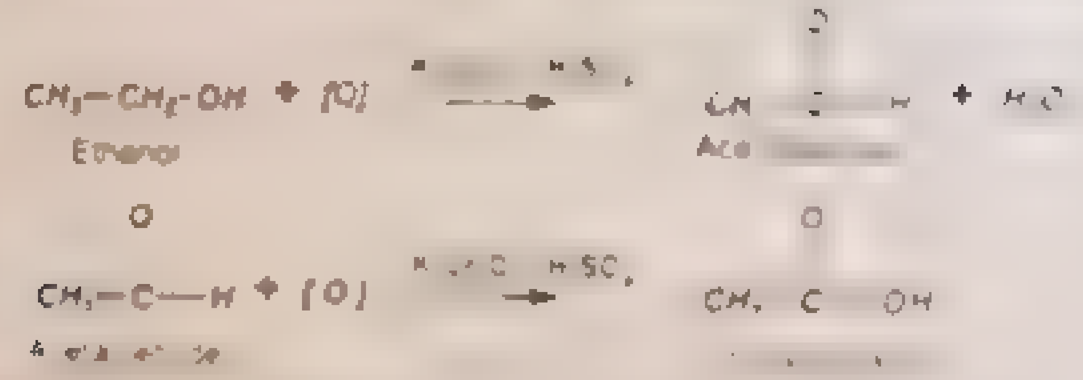
2)

3)

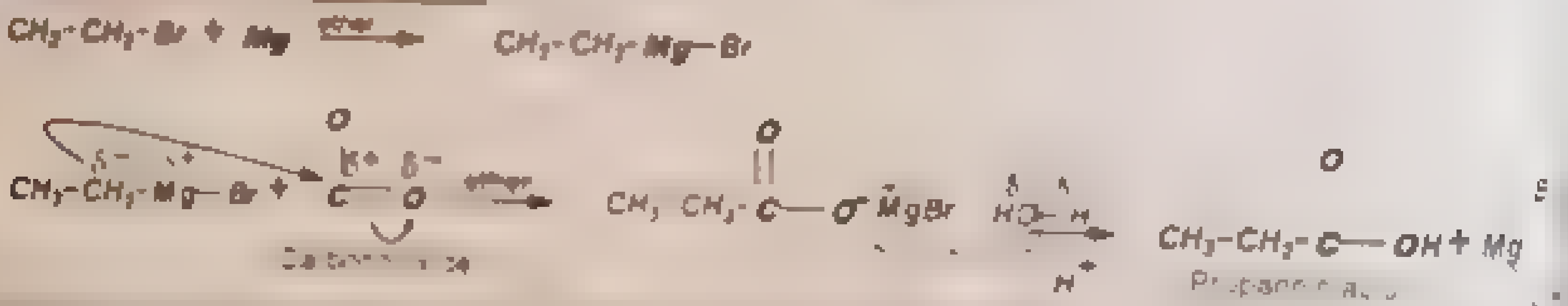
4)

SOME IMPORTANT CONVERSIONS

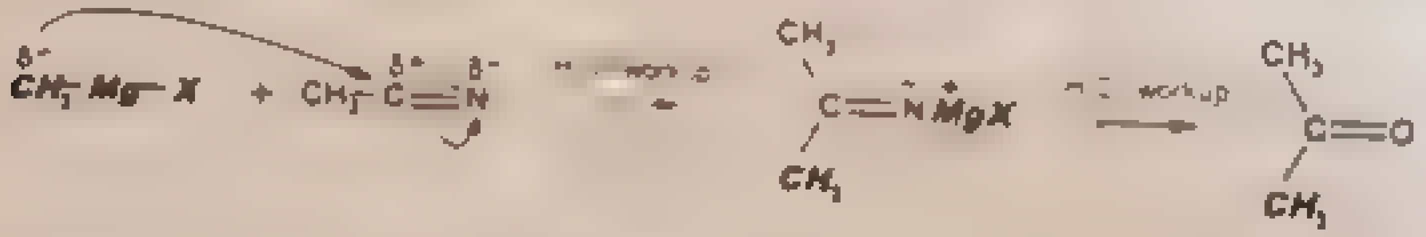
(i) Ethanol into ethanoic acid



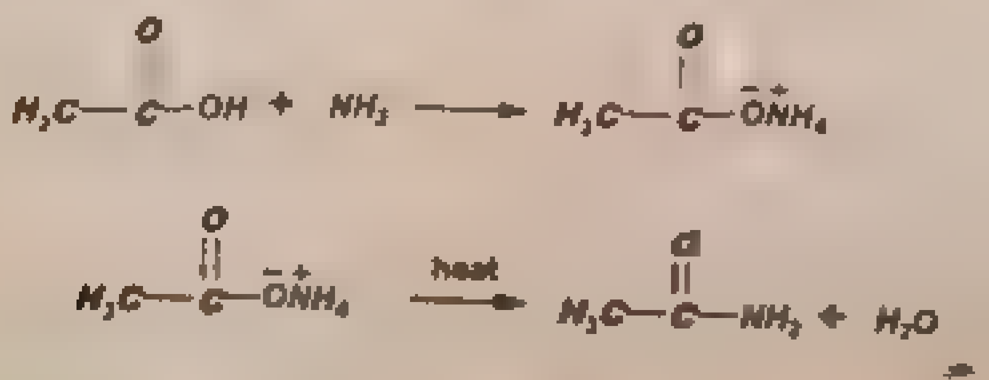
(ii) Ethyl bromide to propanoic acid



(iii) Ethyl magnesium bromide to acetone



(iii) Acetic acid to Acetamide



SOCIETY, TECHNOLOGY AND SCIENCE

CARBOXYLIC ACIDS OCCURANCE.

- Sorbic acid
- Caprylic acid is present in coconut
- Lauric acid is also present in coconut
- Myristic acid is present in nutmeg
- Arachidic acid is present in peanut oil
- Citric acid is present in citrus fruits e.g. lemon, limes, grapes, oranges
- Tartaric acid is present in tamarind
- Lactic acid is present in apples, tomatoes an [illegible]
- Acetic acid is present in grapes
- Malic acid is present in green apples and plums
- Benzoic acid is found in berries
- Butyric acid is present in rancid butter
- Caproic acid is present in goat fat
- Caprylic acid is present in milk
- Palmitic acid is present in palm oil
- Stearic acid is present in waxes, animal fats and oils
- Amino acids are the building blocks of proteins
- Acetoacetic acid and pyruvic acid are the [illegible] chemical significance
- Lactic acid is found in sour milk
- Tartaric acid is found in wine
- Acetic acid is found in vinegar

CARBOXYLIC ACIDS AS FOOD PRESERVATIVES

Formic acid is used as preservative for silage including fresh hay and other [illegible] feed

Boric acid was used as a food preservative in caviar (a product made [illegible] fish eggs) but its use has been banned now

Salicylic acid its use has been banned now

Benzoic acid is used as a preservative in jams, beer, preserved fruit, pickles, [illegible] desert sauces and syrups

Acetic acid is used as a preservative [illegible] margarine, processed cheese, curry powder, cooking oil

Lactic acid is used as a preservative [illegible] beer, canned foods especially vegetables and fruit, fresh fruit and vegetables

Propionic acid is used as a preservative [illegible] dairy products, particularly in cheese and in baking products

TASTE OF DIFFERENT CARBOXYLIC ACIDS

- Esters are derived from carboxylic acids [illegible] in the presence of hydrochloric acid or sulfuric acid, a process called [illegible]
- Ester flavors are a range of fruity, sugary and sweet [illegible] beer types as a normal part of their brewing process.
- Examples of ester flavors are

  Ethyl formate gives raspberries their characteristic taste

  Ethyl acetate has a bittersweet, wine-like [illegible] taste

  Isoamyl acetate has a taste reminiscent of pears or bananas

  Ethyl propionate has rum like taste (Rum is distilled a[illegible] beverage made from sugarcane byproducts)

  Ethyl butyrate –found in pineapples- tastes like sugar water

Ethyl valerate has apple like taste

Ethyl hexanoate is an apple flavoured ester

Ethyl heptanoate has wine-like od[illegible]

Ethyl octanoate found in pineapples has sweet taste

KEY POINTS

- Carbox[illegible]
- The CO_2H [illegible] lone pairs of the hydroxy[illegible]
- The most important reactions of [illegible]boxylic acid derivatives such as acyl halides, esters and am[illegible]
- Esters can also be made [illegible] especially acyl halides and anhydrides by rea[illegible] presence of a weak base
- Loss of carbon dioxide is called **decarboxylation**
- Simple carboxylic acids rarely undergo decarbox[illegible]
- Esters are less reactive towards **Nu** than aldehydes or ketones
- Carboxylic esters (R_1COOR_2) react with 2 equivalents of orga[illegible] Grignard reagents to give tertiary alcohols
- Amides hydrolyze to the parent carboxylic acid and the appropriate amine
- Amides can be reduced by [illegible] but **NOT** the less reactive $NaBH_4$
- The chemistry of the nitrile functional group ($C \equiv N$) is very similar to that of the carbonyl ($C=O$) of aldehydes and ketones
- Nitriles ($RC \equiv N$) react with Grignard reagents or organolithium reagents to give ketones

EXERCISE

Q1 Select the right answer from the choices given with each question

(i) A carboxyl acid contains functional group.
(a) A Hydroxyl group [illegible]
(c) A Hydroxyl and Carb[illegible]

(ii) From the following carboxylic acids which acid has higher acidity
(a) Ethanoic acid [illegible]

(iii) Which reagent is used to reduce a carboxylic acid?
(a) H_2 Ni (b) H_2 Pt (c) $NaBH_4$ [illegible]

(iv) Stronger acid is
(a) CH_3COOH (b) HCOOH (c) CH_3CH_2COOH (d) $CH_3CH_2CH_2COOH$

(v) Acetamide is prepared by;
(a) Heating ammonium acetate (b) Heating methyl cyanide
(c) Heating ethyl acetate (d) The hydrolysis of methyl cyanide

(vi) Carboxylic acids react with metal to form salts with the evolution of
(a) CO_2 (b) H_2 (c) CO (d) CH_4

(vii) Ethane-1,2-dioic acid is also called
(a) Benzoic acid (b) Oxalic acid (c) Formic acid (d) M[illegible]

(viii) Carboxylic acid can be prepared by the action of Grignard's reagent with
(a) O_2 [illegible]

(ix) The IUPAC name for formic acid is
(a) Methanoic acid (b) Acetic acid (c) Ethanoic acid (d) Butanoic acid

(x) The reaction of alcohol with acetic acid is known as
(a) sponification (b) esterification (c) [illegible]

(xi) Esters are formed by the reaction of carboxylic acids with
(a) alcohols (b) ethers (c) aldehydes (d) Alkyl halides

(xii) Which one of the following has both hydroxyl and carboxylic acid groups?
(a) phenol (b) picric acid (c) phthalic acid (d) [illegible]

(xiii) Which of the following cannot be prepared directly from acetic acid
(a) acetamide [illegible]

(xiv) Reaction between caustic soda and a fat is called
(a) esterification (b) hydrogenation (c) neutralization (d) sp[illegible]

(xv) When a carboxylic acid reacts with alcohol it produces a new class of compounds
(a) ethers (b) esters [illegible]

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (b) A Carboxyl group
A carboxylic acid contains a carboxyl [illegible]

(ii) Ans: (d) Nitroethanoic acid

(iii) Ans: (d) $LiAlH_4$
$LiAlH_4$ reduces carboxylic acids [illegible]

(iv) Ans: (b) HCOOH [illegible]

(v) Ans: (a) Heating ammonium acetate
$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{heat} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(vi) Ans: (b) [illegible]

(vii) Ans: (b) Oxalic acid
COOH
|
COOH (Ethanedioic acid or Oxalic acid)

(viii) Ans: (b) CO_2 [illegible]

(ix) Ans: (a) Methanoic acid
Since Formic acid (HCOOH) contains [illegible] methanoic acid

(x) Ans: (b) esterification [illegible]

(xi) Ans: (a) alcohols

The reaction of carboxylic acid with alcoh[illegible]
This reaction is called esterification reaction

(xii) Ans: (d) Salicylic acid

(xiii) Ans: (a) acetamide

Since reaction of acetic acid with ammonia first [illegible] ammonium acetate. It is then heated to give acetamide.

See also MCQ no [illegible]

(xiv) Ans: (d) saponification

Also see CH#21 Biochemistry for the reaction

(xv) Ans: (b) esters

The reaction of carboxylic acid with alcohol produces an ester.
This reaction is called esterification reaction

Q2: Write short answers

(i) What are aliphatic and aromatic carboxylic acids?

Carboxylic acids are generally of two types
Aliphatic carboxylic acids and aromatic carboxylic acids
The general formula of aliphatic carboxylic acid is

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad \text{where } R = H \text{ or an alkyl group}$$

The general formula of aromatic carboxylic acid is

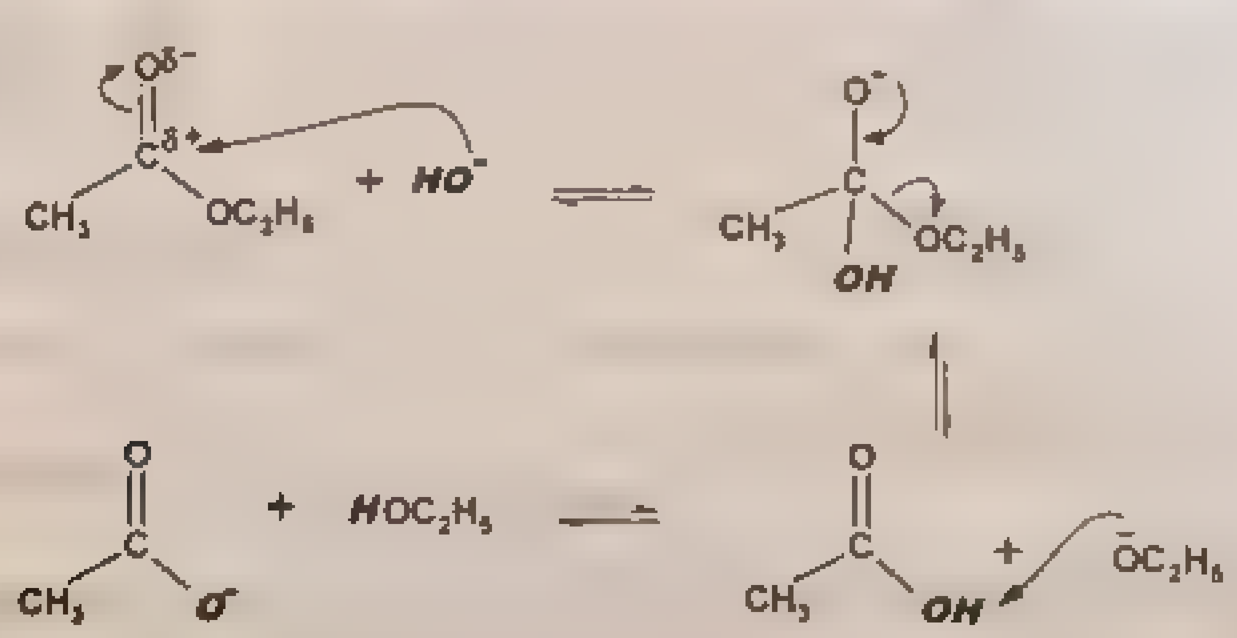
$$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad \text{where } Ar = \text{phenyl or aryl group}$$

(ii) Give probable mechanism of alkaline hydrolysis of an ester

Step 1:
The hydroxide nucleophiles attacks at the electrophilic C of the ester C=O breaking the π bond and creating the **tetrahedral intermediate**

Step 2:
The intermediate collapses, reforming the C=O results in the loss of the leaving group the alkoxide RO leading to the carboxylic acid

Step 3
An acid base reaction. A very rapid equilibrium where the alkoxide RO functions as a base deprotonating the carboxylic



acid RCO_2H ,an acidic work up would allow the carboxylic acid to be obtained from the reaction

A carboxylic acid does not form phenyl hydrazone when treated with phenyl hydrazine. Explain

Hydrazine contains has $-NH_2$ groups. This group accepts proton from carboxylic acid with the help of one lone pair of nitrogen atom. Since lone pair has been used up. Moreover the carbonyl group of carboxylic acid is less electrophilic. So hydrazine cannot attack as nucleophile on carboxylic acid. Thus hydrazone is not formed.

Give the mechanism for the acid catalyzed hydrolysis of a nitrile?

Page 37?

Why acetic acid is often called Glacial acetic acid?

Pure acetic acid freezes to an ice like solid at 17°C. Therefore it is called glacial acetic acid.

What is use of esters?

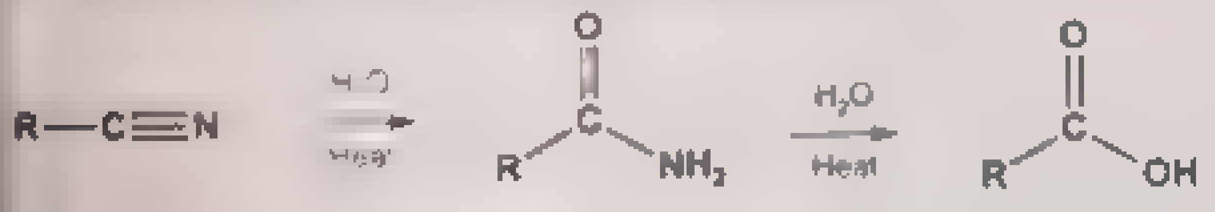
Esters have fruity smell. Thus they are used as artificial flavours.

Flavours of some esters are given below

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octyl acetate	Orange

How may nitriles be converted into carboxylic acid?

The nitriles on hydrolysis yield carboxylic acids via amides



What are acidic amino acids give example?

Amino acids containing more carboxyl group than amino group are called acidic amino acids.

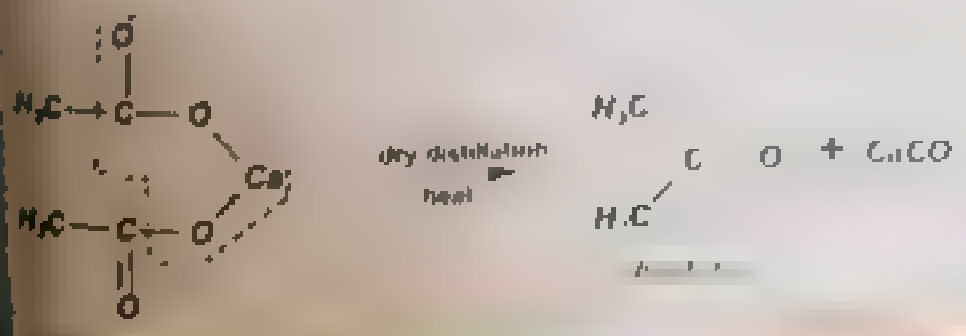
Examples

HOOC — CH_2 — CH — COOH HOOC — CH_2 — CH_2 — CH — COOH

NH_2 NH_2

Aspartic acid Glutamic acid

What happened when ammonium acetate and calcium acetate is heated



x How does carboxylic acids exist in nonpolar solvent

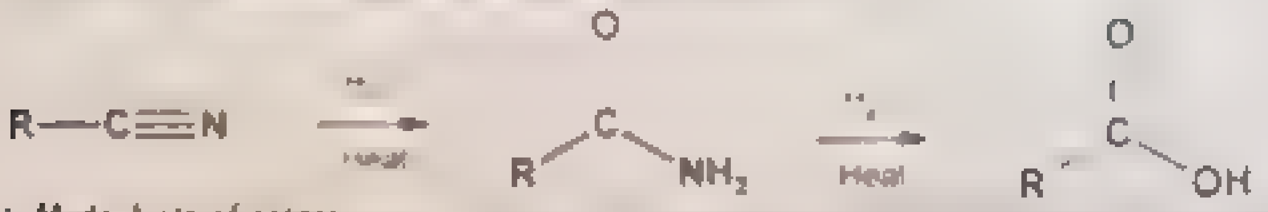
The carboxylic acids exist as dimers in non polar solvent like benzene. Thus [illegible] appears to be twice of their actual mass

Q3: Give detailed answers for the following questions.

(i) How will you prepare carboxylic acids from?

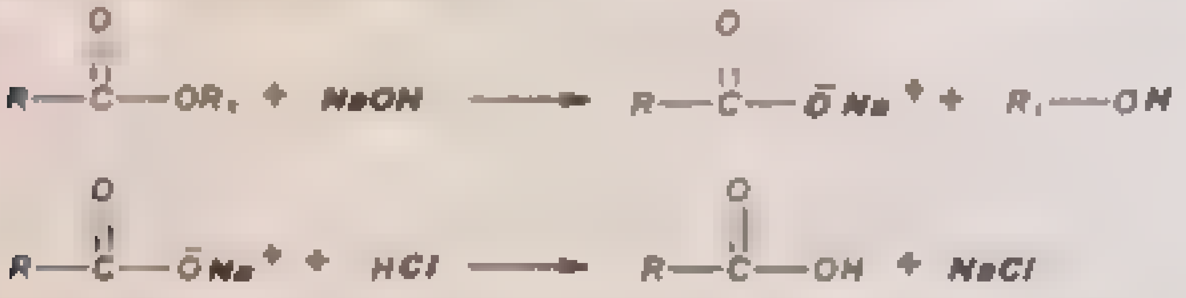
(a) alkyl nitrile

The nitriles [illegible]



(b) Hydrolysis of esters

The ester on boiling with [illegible] sodium hydroxide gives [illegible] acid which on [illegible] dilute HCl gives free carboxylic acid

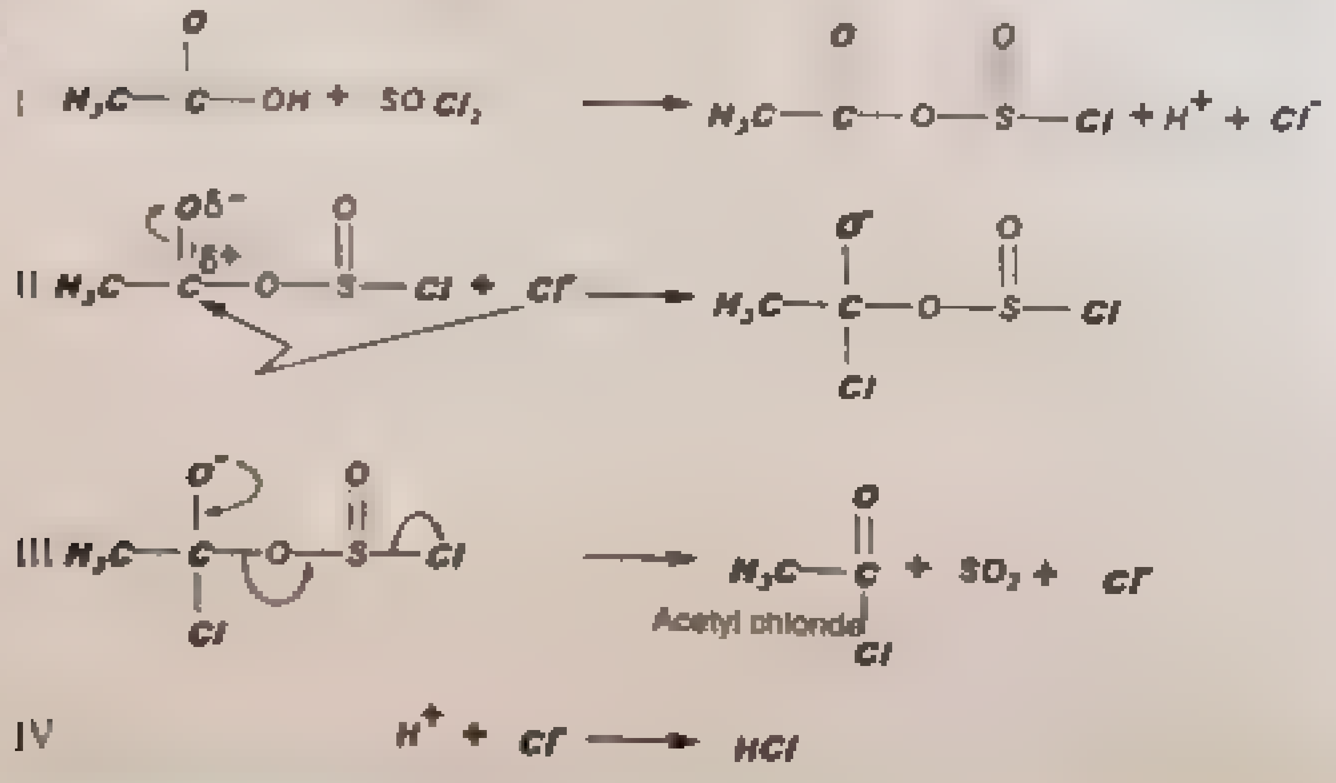


(ii) Give the reaction of acetic acid with the following along mechanism

(a) $SOCl_2$

Acyl chlorides are prepared by treating the carboxylic acid with [illegible] $SOCl_2$ in the presence of a base

Mechanism

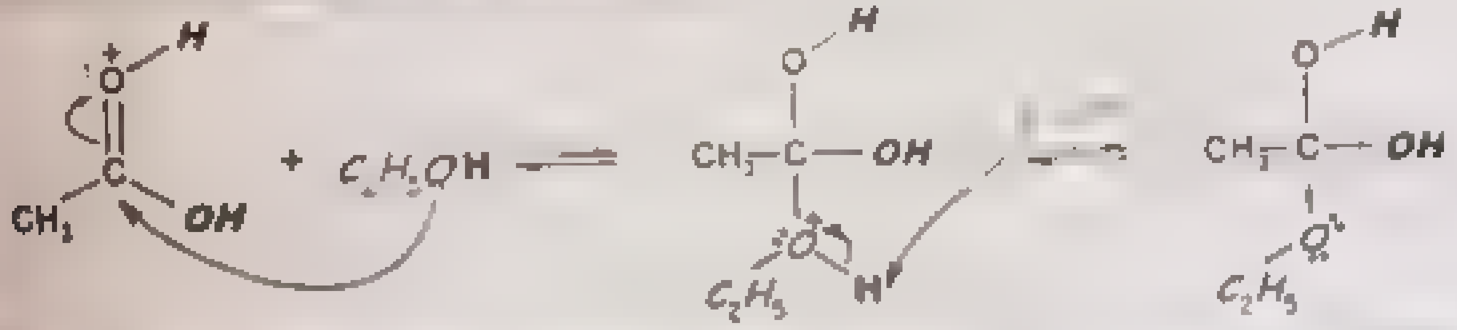


(b) Ethanol

Step 1
An acid base reaction. Protonat...

Step 2:
The alcohol O functions as the nucleophile attack... C=O with the electrons moving towards the oxonium ion, creating the tetrahedral int...

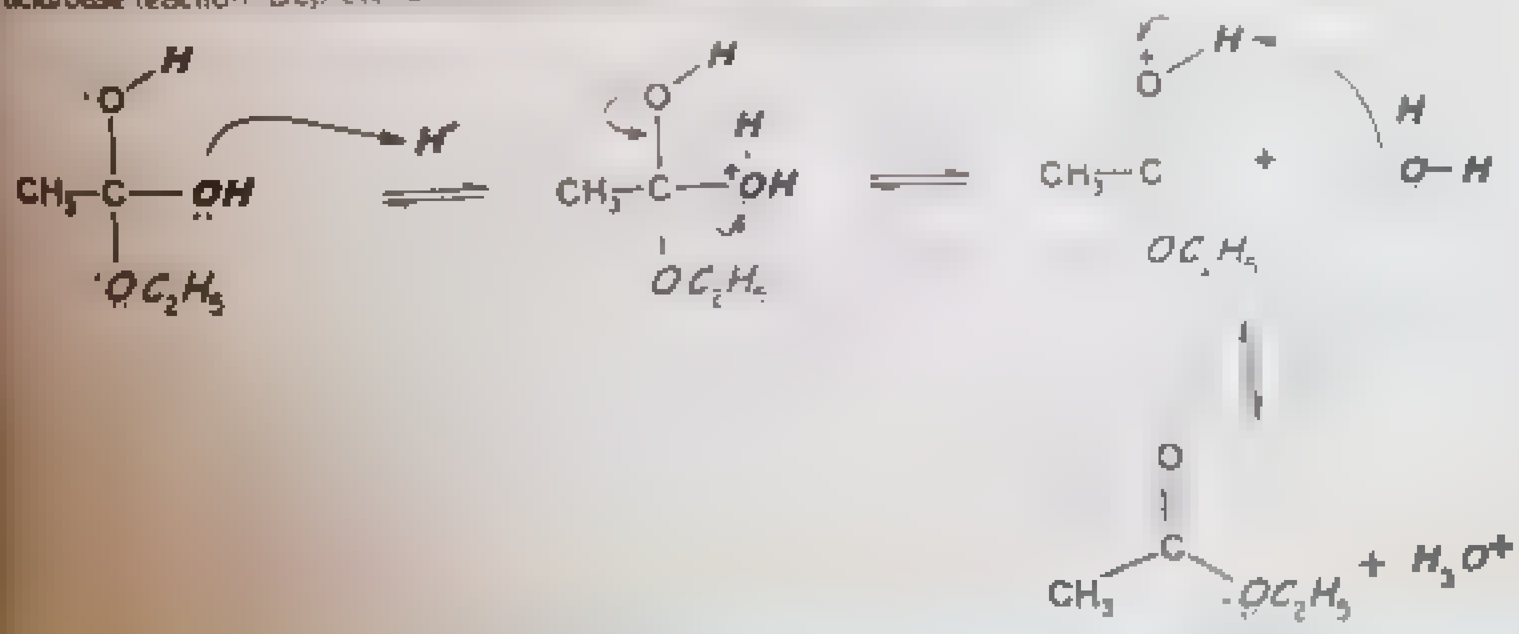
Step 3:
An acid/base reactio...



Step 4:
An acid/base reaction. Need to make ... good leaving group by protonation.

Step 5:
Use the electrons of an adjacent oxygen to help "push out" the lea... water molecule

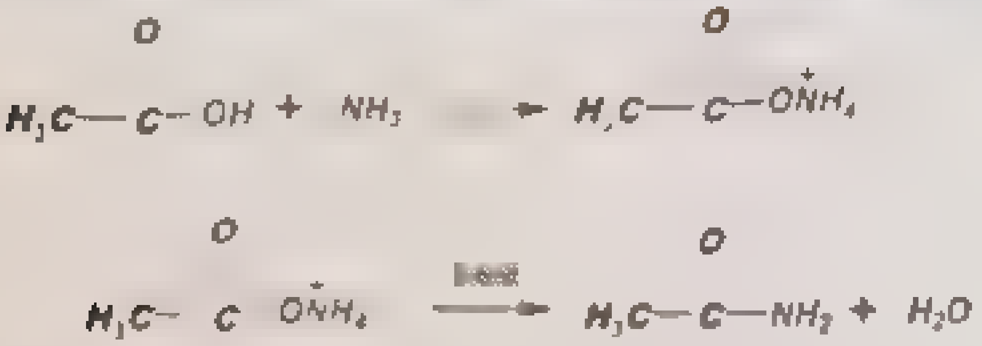
Step 6:
An acid/base reaction. Deprotonat... yl in the ester product



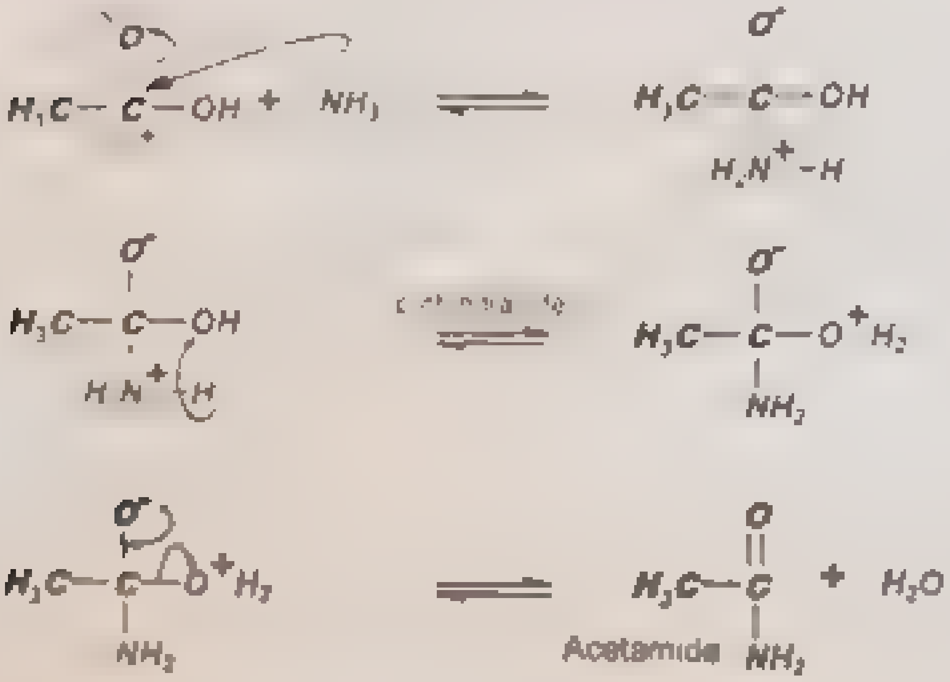
Ethyl acetate

(c) NH_3

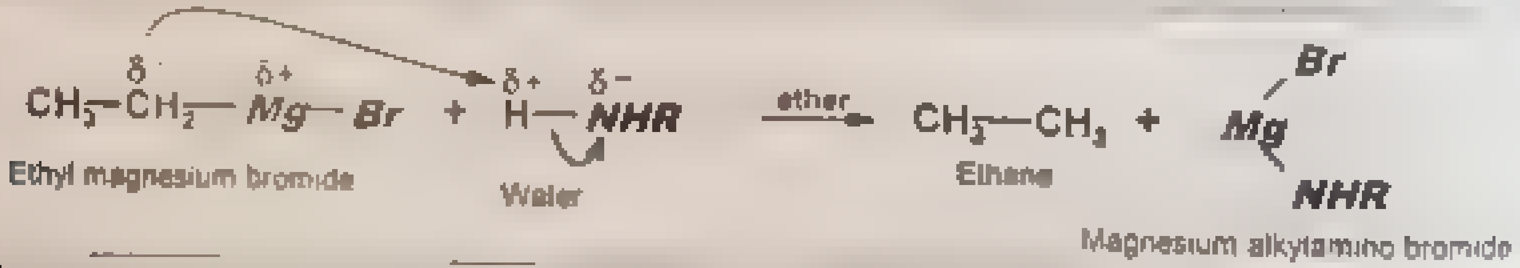
Carboxylic acids react with ammonia to form ammonium salts which on heating produce acid amides



Mechanism

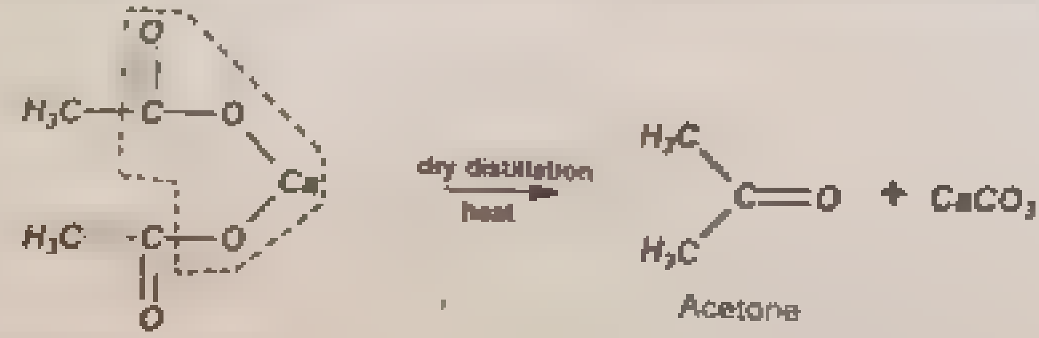


(iii) Give the reaction of amine with Grignard reagent with mechanism



(iv) What happens when following compounds are heated:

(i) **Calcium acetate**



(ii) **Sodium formate and soda lime**

(iii) **Ammonium acetate**

$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{heat} \underset{\text{Acetamide}}{H_3C-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

(v) What is vinegar? Describe how is vinegar prepared from ethanol

The dilute aqueous solution of acetic acid is known as vinegar. Acetic acid can be prepared by the oxidation of ethanol.

$$\underset{\text{Ethanol}}{H_3C-CH_2-OH} + [O] \xrightarrow{K_2Cr_2O_7 + H_2SO_4} \underset{\text{Acetaldehyde}}{H_3C-CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{H_3C-COOH}$$

In industry, acetic acid is also prepared by the fermentation of ethanol with the help of acetic acid bacteria

(vi) Write down the mechanism of the following reactions

1. **Between acetic acid and ethanol**
   Page 381
2. **Between acetic acid ammonia**
   Page 382
3. **Between acetic acid and thionyl chloride**
   Page 380

(vii) How would convert the following?

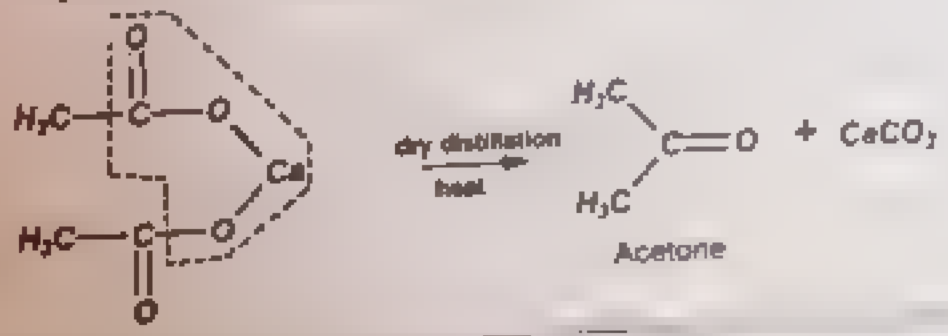
Acetic acid into acetamide

$$\underset{\text{Acetic acid}}{H_3C-\overset{O}{\overset{\|}{C}}-OH} + NH_3 \longrightarrow H_3C-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4$$

$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{N}H_4 \xrightarrow{heat} \underset{\text{Acetamide}}{H_3C-\overset{O}{\overset{\|}{C}}-NH_2} + H_2O$$

Acetic acid into acetone

$$2\,CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2\,H_2O$$



(viii) How amides are reduced with $LiAlH_4$? Give mechanism.

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(ix) What is Friedal & Craft's reaction? Explain their mechanism.

Page 196-197

(x) Give mechanism for reaction for acid catalysed esterification.

Page 381

TEST YOUR SKILLS

Marks:

OBJECTIVE

Time: 20 Minutes

Marks: 17

Note: ... using lead pencil will result in loss of marks

Q1 Circle the correct option i.e. A B C D. Each part carries one mark

(i) Vinegar is
 A. 4-5 % acetic acid B. Glacial acetic acid C. Pure acetic acid D. Any one of these

(ii) Which of the following is not a fatty acid?
 A. Phthalic acid B. Benzoic acid C. Phenyl acetic acid **D. All of above**

(iii) In Fischer esterification, the reactivity order of alcohols is
 A. $CH_3OH > 1° > 2° > 3°$ B. $1° > 2° > 3° > CH_3OH$ C. 3° > 2° > 1° > CH_3... D. H_3...

(iv) Acetic acid at low temperature freezes and called
 A. 90% acetic acid **B. Glacial acetic acid** C. Semi solid acetic acid D. None of above

(v) Which one of the following acid is used for the preparation of synthetic rubber
 A. Carbonic acid B. Formic acid **C. Acetic acid** D. Butyric acid

(vi) 2-Hydroxy propanoic acid is called
 A. Oxalic acid **B. Lactic acid** C. Citric acid D. Aspartic acid

(vii) Carboxylic acid on reduction with HI and red phosphorous gives
 A. Alkanes B. Alkenes C. Alkynes D. Alcohols

(viii) The carbonation of Grignard's reagent is used to prepare
 A. acid halides B. amides **C. carboxylic acids** D. esters

(ix) Which of the following do not contain COOH group
 A. Picric acid B. P-toluene sulphonic acid **C. Both** D. None

(x) An acid chloride compared with its acid boils at
 A. Low temperature B. Higher temperature C. Similar temperature D. An indefinite temperature

(xi) Reaction between caustic soda and a fat is called
 a. esterification (b) hydrogenation (c) neutralization **(d) saponification**
 A. Acidic amino acid B. Basic amino acid C. Neutral amino acid D. All of above

(xii) The reduction of nitriles gives
 A. alcohols **B. amines** C. ester D. None

(xiii) Which is the strongest acid
 A. Cl_3CCOOH B. HCOOH C. $ClCH_2COOH$ D. CH_3COOH

(xiv) The reduction of esters with $LiAlH_4$ gives
 A. Amino acids B. amide **C. alcohol** D. alkane

(xv) Which of the following derivative of carboxylic acids is the most reactive?
 A. acid halides B. amides C. anhydrides D. esters

(xvi) Catalyst used for preparation of anhydride is
 A. $K_2Cr_2O_7$ B. H_2SO_4 **C. P_2O_5** D. V_2O_5

(xvii) The odour of esters is
 A. Pungent B. Suffocating C. Pleasant **D. Fruity**

SUBJECTIVE

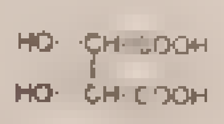
Time: 2.35 Hours

Total Marks Section B and C: 68

Section – B (Marks 42) (14 × 3 = 42)

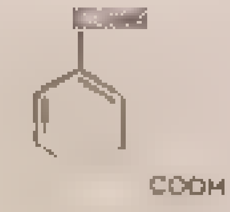
Q2 Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines

(i) Name the following compounds according to IUPAC system 03



a

b



c

(ii) Acetic acid is a component of vinegar
 a. How is Acetic acid manufactured from Acetylene? 02
 b. What is glacial acetic acid? 01

(iii) Esters formed from carboxylic acids give different flavours. What type of flavours is given by Amylacetate, isobutyl formate, Benzylacetate 03

(iv) a. How is acetic acid prepared from alkyl nitriles? 01
 b. Give the mechanism for the reaction of acetic acid with $SOCl_2$ 02

(v) Write the structural formula of the following. 03
a. Acrylonitrile b. Acetophenone c. Adipic acid

(vi) What is Fisher esterification? Give mechanism. 03

(vii) Predict the product of the following reactions:

a. $CH_3COOH + HI \xrightarrow{P}$

b. $R-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow[HCl]{NaNO_2}$

c. $CH_3COOH + NaHCO_3 \longrightarrow$

(viii) a. What are lactones? 01
b. Why methanoic acid is usually called formic acid? 01
c. Why low molecular mass carboxylic acids are water soluble while high mol. mass are insoluble? 1

(ix) a. Write the reactivity order of functional derivatives of carboxylic acids. 1.5
b. What are acid anhydrides, how they are formed? 1.5

(x) a. Describe the acidity of carboxylic acids? 03

(xi) a. How may amides be prepared? 01
b. Describe the mechanism of decarboxylation of dicarboxylic acids 02

(xii) a. How ethanol is converted into acetic acid? 01
b. What is nucleophilic acyl substitution? Give example 02

(xiii) a. What are dicarboxylic acids? 1.5
b. Describe the structure of a COOH group? 1.5

(xiv) a. How the acid by product such as HCl is removed from the solution?
b. Why acetic acid is often called glacial acetic acid? 1.5

(xv) a. Molecular mass of carboxylic acid appears double in a non polar solvent. Why? 02
b. What happens when acid anhydrides are treated with alcohol 01

(xvi) a. How α-amino acids can be converted into α-hydroxyl acids? 01
b. Write two chemical reactions in which carboxyl group of carboxylic acid is involved? 02

(xvii) a. How would you convert acetic acid into Acetamide? 1
b. What happened when calcium acetate is heated? 01
c. How may nitriles be converted into carboxylic acid?

(xviii) How does acetic acetic reacts with the following?
a. Methanol b. PCl_5 c. $LiAlH_4$

(xix) What happens when
a. Sodium metal is droped in acetic acid
b. Sodium formate is heated at high temperature in presence of soda lime
c. What is oxonium ion?

Section C

Note: Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

Q. 2. a. How will you prepare carboxylic acids from?
(i) Alkyl nitriles (ii) Hydrolysis of esters

b. Give the [illegible]
$SOCl_2$ [illegible]

c. What kind [illegible]

d. How nitriles are prepared?

Q 4. a. How would you convert Acetic acid into the following compounds? (4)
i. Methane [illegible]

b. Discuss [illegible]

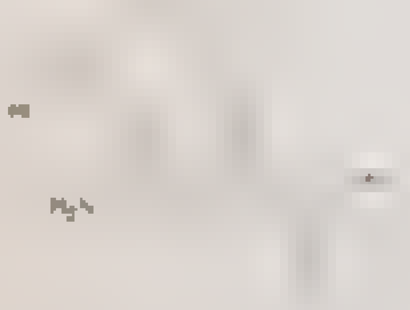
c. Write [illegible]

Q 5. a. Write the mechanism of reaction of a Grignar [illegible]

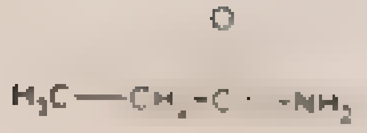
b. Give the IUPAC names of the following comp[illegible]

(i)

(ii)



(iii)

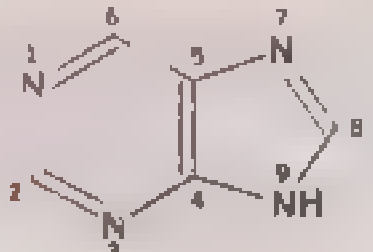


(iv) Adipic acid

(v) Valeric acid

c. How may acid halides be converted into different [illegible] (4)

CHAPTER # 21
BIOCHEMISTRY



Purine

INTRODUCTION TO BIOCHEMISTRY

Biochemistry is the branch of science concerned with studying the various molecules that occur in living cells and organisms, with their chemical reactions.

- Biochemistry is a hybrid science
- Biology is the science of living organisms and chemistry is the science [illegible] so biochemistry is the science of the atoms and molecules in living organisms
- Biochemistry is concerned with the complete spectrum of all forms of [illegible] simple viruses and bacteria to complex human beings.
- It attempts to describe the structures, mechanisms, and chemical processes [illegible] organisms [illegible] molecular level
- Living organisms should be able to transform matter and energy into different forms, show response to changes in their environment and show growth and reproduction

MACROMOLECULES

Molecules containing large number of atoms and high molecular mass are called macromolecules

- All living organisms undergo changes due to large organic compounds [illegible]
- Four main types of macromolecules control all activities. They are [illegible] acids.

CARBOHYDRATES

Old Definition

Carbohydrates are called carbohydrates because they contain carbon, oxygen [illegible] generally in proportion to form water with the general formula [illegible]

Modern Definition:

Carbohydrates are polyhydroxy compounds of aldehydes or ketones

Remember!

All the organic compounds containing hydrogen and oxygen in the [illegible]

e.g.

(i) Formaldehyde HCHO $C(H_2O)$
(ii) Acetic acid CH_3COOH [illegible]
(iii) Lactic acid $CH_3CHOHCOOH$ [illegible]

On the other hand, Rhamnose ($C_6H_{12}O_5$) does not have the ratio [illegible] carbohydrate

Importance of Carbohydrates

- Carbohydrates or saccharides are the most abundant of the four types of macromolecules
- These are sugars or starches
- They have several roles in living organisms [illegible] components of plants and arthropods
- Carbohydrate derivatives are actively involved in fertilization [illegible] clotting and growth

- Most organic matter on earth is made up of carbohydrates because they are involved in so many ... including
  - ✓ Energy stores, fuels, and metabolic intermediates
  - ✓ Ribose and deoxyribose sugars are part of the structural framework of RNA and DNA
  - ✓ The cell walls of bacteria are mainly made up of polysaccharides types of carbohydrate
  - ✓ Cellulose (a type of carbohydrate) makes up most of plant cell walls
  - ✓ Carbohydrates are linked to many proteins and lipids where they are vitally involved in interactions

CLASSIFICATION OF CARBOHYDRATES

Exercise Q3 (i) Describe different classes of Carbohydrates

Carbohydrates are classified into three types

MONOSACCHARIDES

Definition: *The carbohydrates which do not hydrolyze to simpler units are called monosaccharides*

This is the smallest possible sugar unit

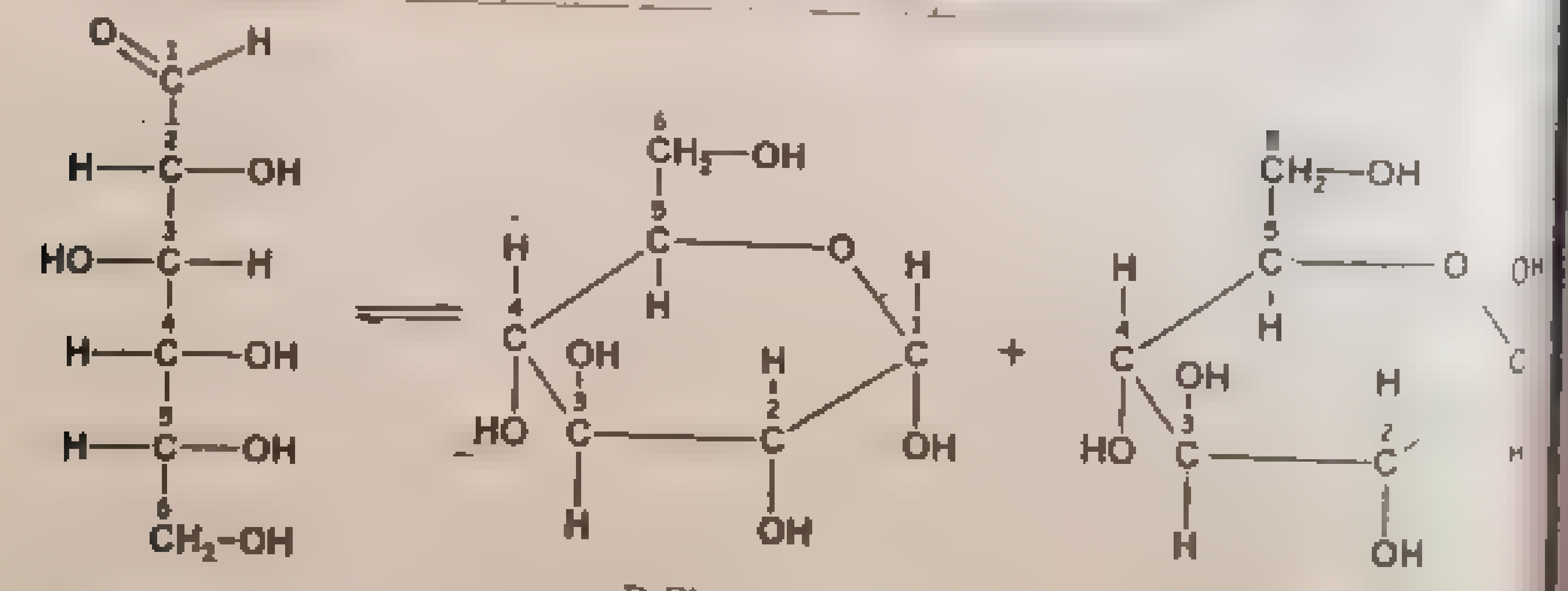
- The term blood sugar refers to glucose in the blood
- Glucose is a major source of energy for a cell
- Glucose is naturally in honey and corns
- In human nutrition, galactose can be found most readily in milk and dairy products
- Fructose is found mostly in vegetables and fruits grapes.
- When monosaccharides join together in linked groups, they are called polysaccharides

Examples: glucose, galactose or fructose

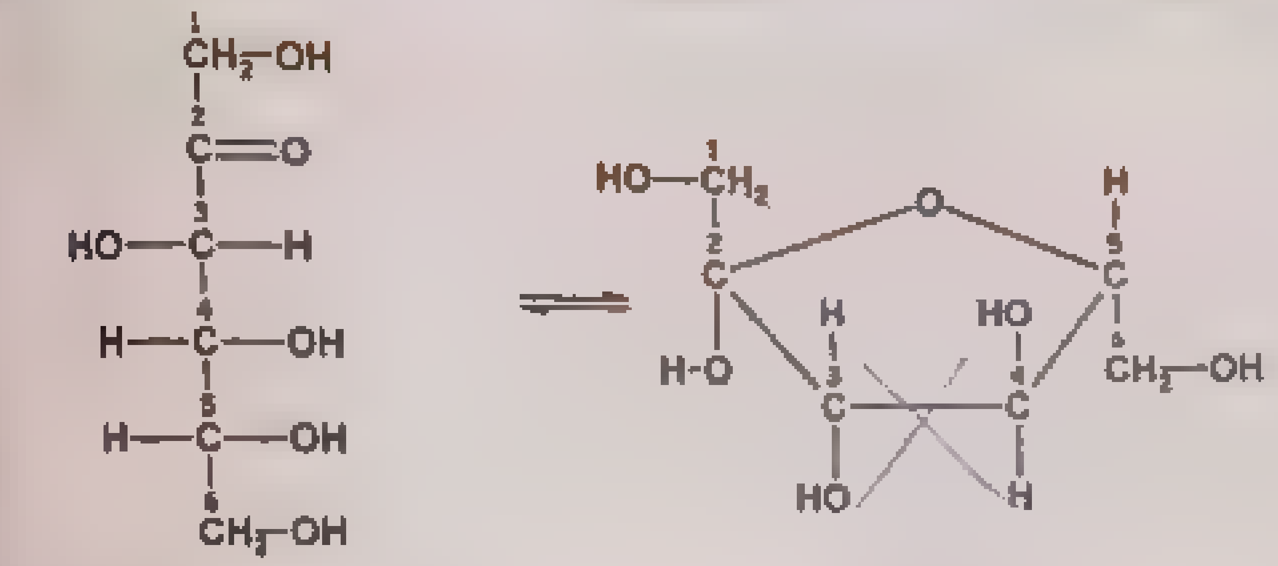
CLASSIFICATION OF MONOSACCHARIDES

- Monosaccharides can be further classified by the number of carbons present
- Among these hexoses (6-carbons) are most common

Number of Carbons		
Six = Hexose	Five = Pentose	Three = Triose
Glucose	Ribose	Glyceraldehyde
Galactose		
Fructose		



D-Glucose (open chain form) α–D-Glucose β–D-Glucose (cylic form)



D-Fructose
(open chain form) (cylic form)

DISACCHARIDES

Definition: *Carbohydrate producing two monosaccharide units on hydrolysis are called disaccharides*

- In these two monosaccharide molecules are bonded together to form disaccharides
- Disaccharides are polysaccharides. The term "poly" specifies any number higher than one while "di" specifies exactly two

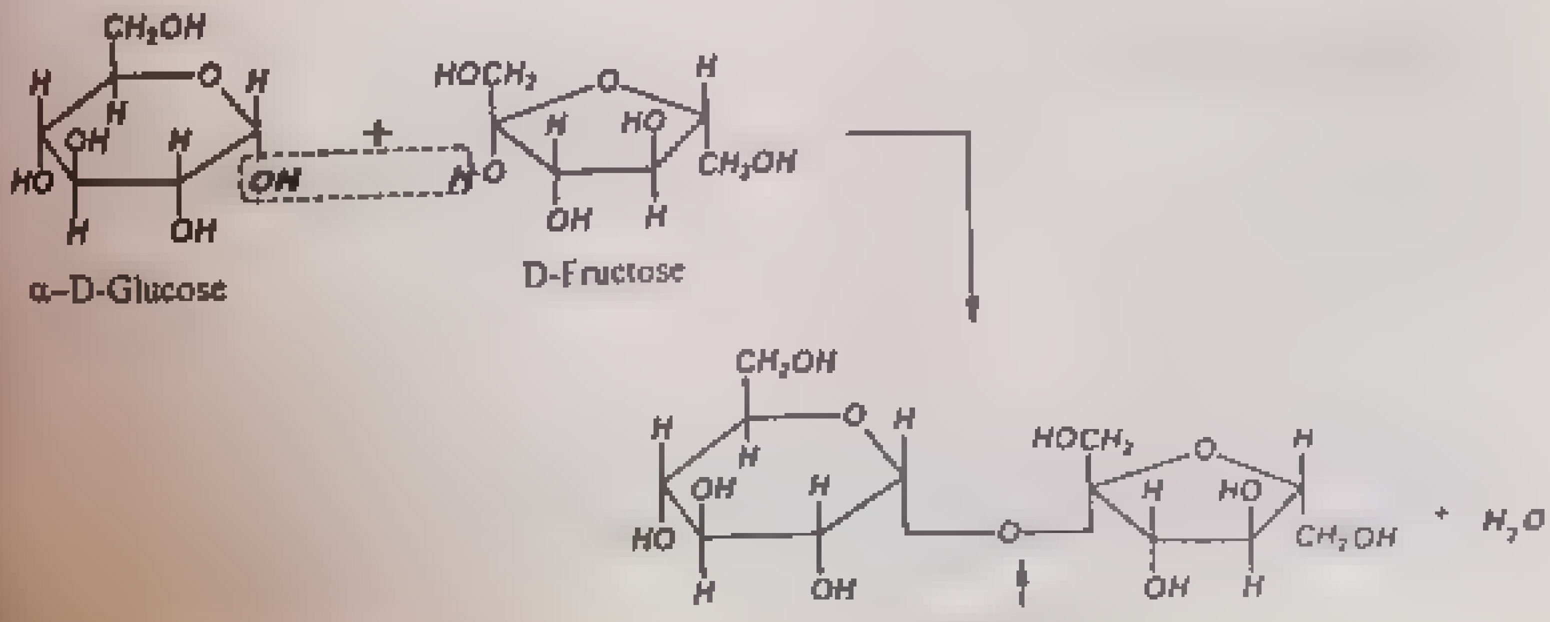
Examples: lactose, maltose, and sucrose.

Occurrence:

- Lactose is formed in the milk
- Sucrose occurs in sugarcane, sugar beet, mango, pineapple, almond and apricot

How the monosaccharides combine with each other:

The OH group of one monosaccharide molecule acts as alcohol. It forms a glycosidic linkage with the hemiacetal group of second monosaccharide molecule. In this way glucoside is produced which is called disaccharide. Thus, disaccharides are the acetals formed from two monosaccharides by the elimination of one molecule of H_2O molecule as shown below.



Glycosidic linkage
Sucrose

If one glucose molecule is bonded with a galactose molecule, lactose is formed, ...

POLYSACCHARIDES

Definition: The [illegible] polysaccharides [illegible]

- [illegible] The chain may be branc[illegible]
- P[illegible] [illegible] thousands of monosaccharides
- P[illegible] a complex compound is a po[illegible] [illegible]

Examples: Starch, cellulose etc

A brief summary is presented below:

Carbohydrates		
Monosaccharides	**Disaccharides**	**Polysaccharides**
[illegible]	Sucrose	Starch
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
Ribose		
Glyceraldehyde		

Interesting Information

A new system for classifying carbohydrates is the glycemic index. The glycemic index ranks [illegible] affect blood sugar level by measuring how much the blood sugar increases after one eats.

FUNCTIONS OF CARBOHYDRATES

The main functions of carbohydrates are given below:

- They are source of energy. Thus, they spare protein so that protein can concentrate on building, repairing [illegible] maintaining body tissues instead of being used up as an energy source.
- For proper fat metabolism, carbohydrates must be present. If there are not enough carbohydrates, [illegible] amounts of fat are used for energy. The body is not able to handle this large amount so quickly [illegible] accumulates ketone bodies, which make the body acidic. This causes a condition called ketosis.
- Carbohydrate is necessary for the regulation of nerve tissue. These are the only source of energy for the [illegible]
- Certain types of carbohydrates support the growth of healthy bacteria in the intestines for digestion.
- Some carbohydrates are high in fibre. These helps prevent constipation. These also lowers the risk [illegible] diseases such as cancer, heart disease and diabetes.
- Polysaccharides act as food stores in plants in the form of starch, or in humans and other animals in the form [illegible] glycogen.
- Polysaccharides also have structural roles in the plant cell wall in the form of cellulose or pectin and the [illegible] outer skeleton of insects in the form of chitin.

THREE MAJOR FUNCTIONS OF CARBOHYDRATES

Three major functions of polysaccharides are discussed below

1. STORAGE POLYSACCHARIDES

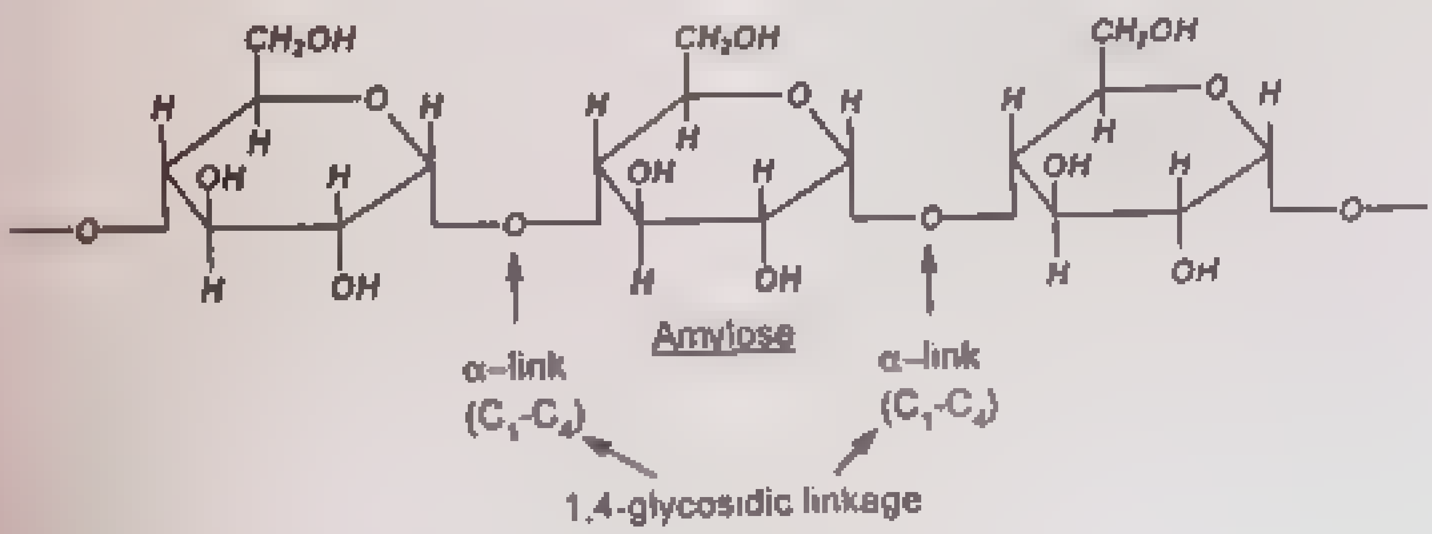
Glycogen:

- The carbohydrates are stored as glycogen in humans and animals
- It is a polysaccharide that is stored in the liver and muscles.

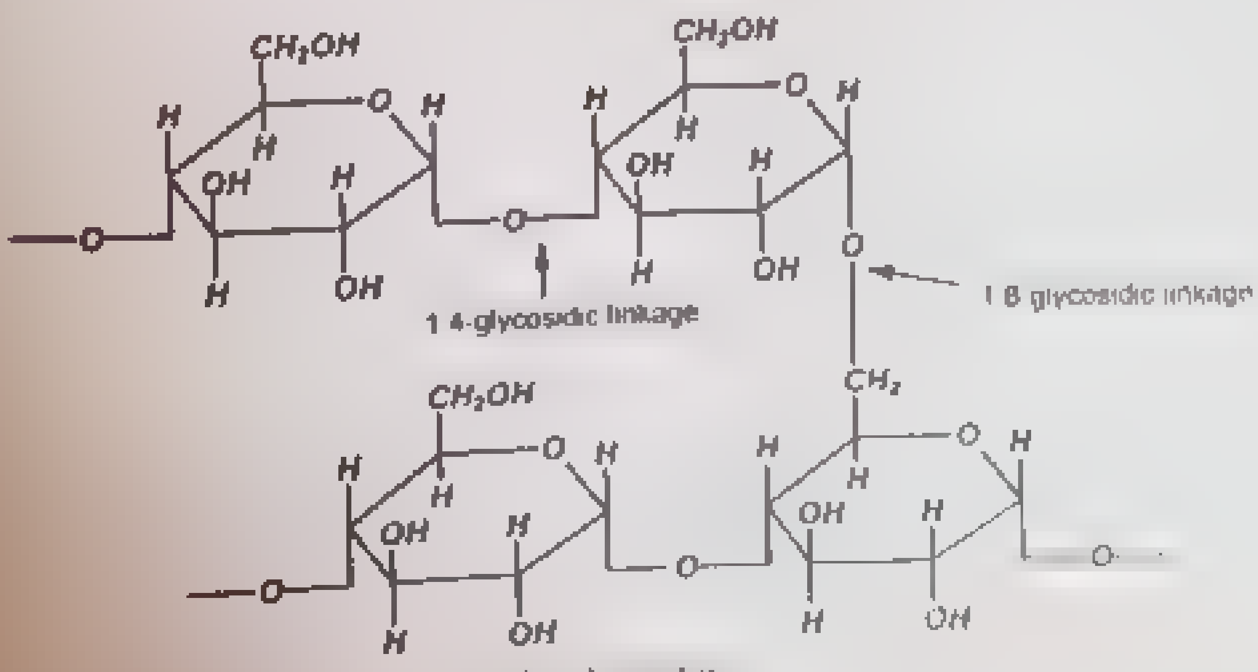
Starch:

- These are glucose polymers made up of Amylose (10-20%) and Amylopectin (80-90%
- Starches are water insolubie.
- Humans and animals digest them by hydrolysis. Our bodies have amylases which break them down
- Rich sources of starches for humans are potatoes, rice and wheat

Structures of Amylase and Amylopectin are given below



Amylose

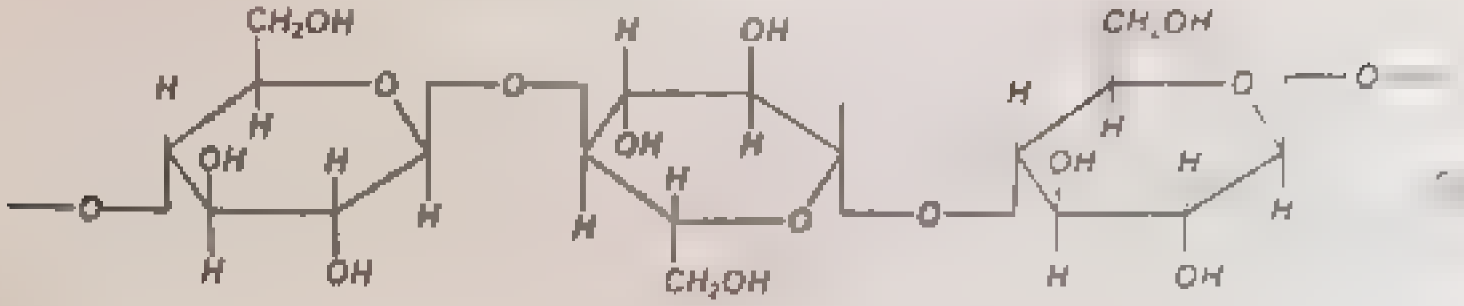


Amylopectin

(2) STRUCTURAL POLYSACCHARIDES

Cellulose

- The structural constituents of plants are made mainly fr
- Wood is mostly made of cellulose
- Paper and cotton are almost pure cellulose



Chitin:

- It is one of the most abundant natural materials in the world
- Microorganisms such as bacteria and fungi secrete chitinases which
- Chitin is the main component of fungi cell walls the exoskeletons crabs, lobsters, ants, beetles, and butterflies

(3) BACTERIAL POLYSACCHARIDES

- They are found in bacteria, especially in bacterial capsules
- Pathogenic bacteria often produce a thick layer of mucous like polysaccharide from the host's immune system
- Thus, if the bacteria are in a human then human's immune system would less likely attack the bact the polysaccharide layer covers its pathogenic properties

NUTRITIONAL IMPORTANCE OF CARBOHYDRATES

- Scientific research has shown the diverse functions of carbohydrates in the body and their
- Bread pasta beans, potatoes, bran rice and cereals are carbohydrate rich foods

Remember!

- *1 gram of carbohydrate contains approximately 4 kilocalories (kcal)*
- *1 gram of protein contains approximately 4 kcal*
- *1 gram of fat contains approximately 9 kcal*

(A) BODY WEIGHT REGULATION

People eating a diet high in carbohydrates are less likely to accumulate body fat compared wi follow a low carbohydrate/high-fat diet

It is due to three reasons

(i) It could be due to the lower energy density of high carbohydrate diets, as carbohydrates have few than fats Fiber-rich foods also tend to be bulky and physically filling, so fewer calories may be consumed

(ii) Studies show that carbohydrates, both in the form of starch and sugars, work quickly to aid satiety and those consuming high carbohydrate diets are therefore less likely to overeat

(iii) It is evident that diets high in carbohydrate, as compared with those high in fat, reduce the likelihood developing obesity

Interesting Information

- *In several studies, high sugar consumers have been found to be slimmer than low sugar consumers*
- ***Obesity** means having too much body fat*

(B) DIABETES

- There is no evidence that sugar consumption is linked to the development of any type of diabetes.
- There is now a good evidence that obesity and physical inactivity increase the likelihood of developing non insulin dependent diabetes, which usually occurs in middle age.
- Weight reduction is usually necessary and is the primary dietary aim for people with non-insulin dependent (Type II) diabetes.
- Consuming a wide range of carbohydrate foods is an acceptable part of the diet of all diabetics, and the inclusion of low glycaemic index foods is beneficial as they help to regulate blood glucose control.
- Most recommendations for the dietary management of diabetes allow a modest amount of ordinary sugar as the inclusion of sugar with a meal has little impact on either blood glucose or insulin concentrations in people with diabetes.

(C) DENTAL HEALTH

Factors Affecting Tooth Decay

The incidence of tooth decay is influenced by a number of factors. These include:

- degree of oral hygiene and plaque removal carried out
- availability of fluoride,
- type of food eaten,
- frequency of consumption of any fermentable carbohydrate
- genetic factors

Role of Carbohydrates in Tooth Decay

- Foods containing sugars or starch can be broken down by the enzymes and bacteria in the mouth. This produces acid which attacks the enamel of the teeth.
- The important thing is the often use of carbohydrate not the amount of sugar or other carbohydrate.
- After an acid challenge, saliva provides a natural repair process which rebuilds the enamel.
- When carbohydrate-containing foods are consumed too frequently or chewed over time, this natural repair process is overcome by the tooth decay process. Thus the risk of tooth decay is increased.

(D) GETTING ACTIVE

- There is now substantial evidence that carbohydrates can improve the performance of athletes.
- During high intensity exercise, carbohydrates are the main fuel for the muscles.
- By consuming high levels of carbohydrate before, during and after training [illegible] well stocked. These stocks help the athlete to perform for longer and help their [illegible]
- The vital role of physical activity in maintaining health and fitness [illegible] There is no doubt that many people would benefit from increasing their [illegible] of body weight. It also reduces the risk of developing diseases such as heart disease and [illegible] want to keep fit and active, a well balanced high carbohydrate diet is recommended.

QUICK QUIZ-1

(1) What are carbohydrates? Give its general formula.

Old Definition

Carbohydrates are called carbohydrates because they contain [illegible] generally in proportion to form water with the general formula [illegible]

Modern Definition:

Carbohydrates are polyhydroxy compounds of aldehydes or ketones [illegible] be assigned some general formula.

2) Quote one example of each type of carbohydrates

Carbohy [illegible]

Monosaccharides: e.g g[illegible]

Disaccharides: e.g lactose maltose s[illegible]

Polysaccharides: e.g. starc[illegible]

3) Write structural formulae of Glucose and Fructose

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(4) What do you understand by glycemic index?

It is a new system for classifying carbohydrates is the glycemic index

The glycemic index ranks foods on how they affect blood sugar level by measuring how much the blood sugar increases after one eats

(5) How much calories do 1gm of carbohydrate have?

1 gram of carbohydrate contains approximately 4 kilocalories (k[illegible]

(6) On what factors tooth decay depend?

The incidence of tooth decay is influenced by a number of factors. These [illegible]

- degree of oral hygiene and plaque removal carried out
- availability of fluoride
- type of food eaten
- frequency of consumption of any fermentable carbohydrate
- genetic factors

PROTEINS

Definition *The molecules which yield amino [illegible]*

- Proteins are probably the most important class of biochemical molecules, although of c[illegible] carbohydrates are also essential for life
- Proteins are the basis for the major structural components of animal and [illegible]
- Proteins are natural polymer molecules consisting of amino acid [illegible] proteins may range from two to several thousand
- These molecules contain nitrogen, carbon, hydrogen and oxygen
- They act as biological catalysts (enzymes), form structural parts of orga[illegible] recognition factors, and act as molecules of immunity. Proteins can also be a source of fu[illegible]

CLASSIFICATION OF PROTEINS

Three classes of proteins are usually defined

A Simple Proteins

Definition *Those which give one amino acid only upon hydrolysis*

Examples

- **Albumins**
  - ✓ blood (serumbumin), milk (lactalbumin), egg white (ovalbumin), lentils (legumelin), kidn[illegible] (phaseolin), wheat (leucosin)
  - ✓ Globular protein is soluble in water and dilute salt solution
  - ✓ It is precipitated by saturation with ammonium sulfate solution
  - ✓ It is coagulated by heat
  - ✓ It is usually found in plant and animal tissues

- **Globulins.**
  - ✓ blood (serum globulins), muscle (myosin), potato (tuberin), Brazil nuts (excelsin), hemp (edestin), lentils (legumin)
  - ✓ Globular protein is sparingly soluble in water and soluble in neutral solutions
  - ✓ It is precipitated by dilute ammonium sulfate
  - ✓ It is coagulated by heat
  - ✓ It is distributed in both plant and animal tissues

- **Glutelins.**
  - ✓ Wheat (glutenin); rice (oryzenin)
  - ✓ It is insoluble in water and dilute salt solutions
  - ✓ It is soluble in dilute acids
  - ✓ It is found in grains and cereals

- **Histones:**
  - ✓ thymus gland, pancreas and nucleoproteins (nucleohistone)
  - ✓ It is soluble in water, salt solutions and dilute acids
  - ✓ It is insoluble in ammonium hydroxide
  - ✓ It yields large amounts of lysine and arginine
  - ✓ It is present combined with nucleic acids within cells

- **Scleroproteins:**
  - ✓ connective tissues and hard tissues
  - ✓ Fibrous protein is insoluble in all solvents
  - ✓ It is resistant to digestion

B. CONJUGATED PROTEINS.

Definition: *Those which give an amino acid and non protein group upon hydrolysis*

Examples:

- **Nucleoproteins.**
  - ✓ cytoplasm of cells (ribonucleoprotein), nucleus of chromosomes (deoxyribonucleoprotein), viruses and bacteriophages.
  - ✓ It contains nucleic acids, nitrogen and phosphorus
  - ✓ It is present in chromosomes and in all living forms as a combination of protein with either DNA or RNA.

- **Mucoprotein:**
  - ✓ saliva (mucin) and egg white (ovomucoid)
  - ✓ Proteins combined with amino sugars, sugar acids and sulfates

- **Glycoprotein.**
  - ✓ bone (osseomucoid), tendons (tendomucoid) and cartilage (chondromucoid)
  - ✓ If it contains more than 4% then hexosamine, mucoproteins
  - ✓ If less than 4%, then glycoproteins.

- **Phosphoprotein:**
  - ✓ milk (casein) and egg yolk (ovovitellin)
  - ✓ Phosphoric acid joined in ester linkage to protein.

C. DERIVED PROTEINS:

Definition *Those which are derived from simple and conjugated proteins*

Examples:

- ***Proteans:***
  - ✓ edestan (from elastin) and myosin (myosin)
  - ✓ It results from short action of acids or enzymes
  - ✓ It is insouble in water
- ***Proteases.***
  - ✓ Intermediate products of protein digestion
  - ✓ It is soluble in water
  - ✓ It is not coagulated by heat.
  - ✓ It is precipitated by saturated ammonium sulfate
  - ✓ It results from partial digestion of protein by pepsin or trypsin
- ***Peptones:***
  - ✓ Intermediate products of protein digestion
  - ✓ It has the same properties as proteases except that they can not be salted out
  - ✓ It is of smaller molecular weight than proteases
- ***Peptides:***
  - ✓ Intermediate products of protein digestion
  - ✓ Two or more amino acids joined by a peptide linkage.
  - ✓ It is hydrolyzed to individual amino acids.

STRUCTURE OF PROTEINS

Exercise Q3 (ii): Explain the structure of Proteins.

The structure of a protein depends upon the spatial arrangement of polypeptide chains present in proteins

Since three spatial arrangements are possible proteins have the following structures

(A) Primary structure
(B) Secondary structure
(C) Tertiary structure
(D) Quaternary structure

Quick Quiz-2 (2) Differentiate primary, secondary and tertiary structure of Proteins

(A) THE PRIMARY STRUCTURE OF PROTEINS

- The sequence of amino acids in a peptide chain is called primary structure
- Amino acids are linked with one another through peptide bond. The arrangement of these acids is called primary structure

(B) THE SECONDARY STRUCTURE OF PROTEINS

- Peptide chains may acquire spiral shape or may be present in a zig-zag manner This coiling or zig-zagging of polypeptide is called secondary structure of protein.
- It is due to the formation of H-Bonds.

THE TERTIARY STRUCTURE OF PROTEINS

...sing or folding of polypeptide chains represents tertiary struct...

QUATERNARY PROTEINS

- Quaternary means four. This is the ...
- Quaternary protein is the arrangement of multip... subunit complex
- A variety of bonding interactions ... the various chains into a particular geometry

Quaternary protein structure

PROPERTIES OF PROTEINS

(1) Proteins are one of the four major groups of ...

(2) These giant molecules carry out many of the ...

(3) Proteins are involved in such processes as ... manipulation and much more

(4) They are complex, huge associations of molecules ... to understand

(5) Fortunately they are all built using the same construct...

(6) As with all macromolecules, proteins are polymers ... joined together in long chains

(7) There are about 20-22 common amino acids found in most prote... one of these small molecules has the same common structure, but varies in the nature of one chem...

(8) It is the varying structure and properties of these R-groups that ... another

(9) Amino acids are joined together in long chains called "polypeptides" a name which comes fr... bond holding the chains of amino acids together. The group of atoms that ... acids ... called a peptide bond. The order or sequence of amino acids along a polypeptide chain ... critical property of proteins, its primary structure.

IMPORTANCE OF PROTEINS

1
2
3 [illegible]
(4) Hemoglobin [illegible]
(5) Some of [illegible]
(6) Proteins have [illegible] The [illegible]
precipitate [illegible] to be [illegible]
(7) Gelatin is obtained [illegible] skins and [illegible]
(8) Casein is [illegible]
(9) Proteins [illegible] are used for [illegible]

QUICK QUIZ 2

(1) What are proteins? Gi[illegible]

The molecules which [illegible] Proteins.

Proteins are classified [illegible]

Simple Proteins:	*e.g. Albumins, Globulins, Histones*
Conjugated proteins:	*e.g. Nucleoproteins, Gl[illegible]*
Derived proteins:	*e.g. Proteases, Peptones*

(2) Differentiate primary, secondary and tertiary structure of Proteins

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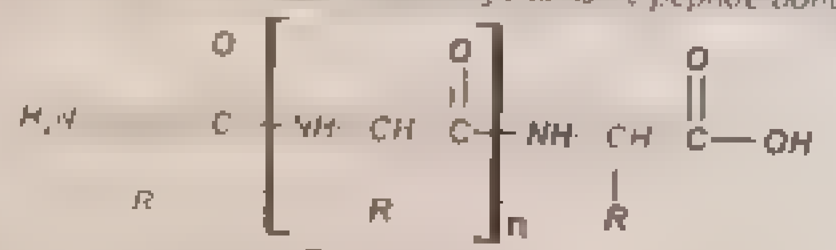
(3) What are polypeptides?

When amino a[illegible] long chains by peptide bond then the [illegible]



Polypeptide

ENZYMES (Greek word En means in and Zyme means yeast)

Definition: [illegible] which alter the speed of metabolic activities in the living bodies

Enzymes are complex protein molecules which are quite specific in action and sensitive to tempera[illegible]

ROLE OF ENZYMES AS A BIOCATALYST

The life of living organisms is a reflection of what is going on in their bodies

- ***Metabolism*** [illegible] biochemical reactions that occur in living organisms in order [illegible] These processes allow organism to grow and reproduce, maintain their structures and respond to environments. It is of two types
  - ✓ ***Anabolism*** [illegible] the biochemical reactions in which larger molecules are synthesized
  - ✓ ***Catabolism*** [illegible] the biochemical reactions in which larger molecules are broken down [illegible] energy is released in **catabolism** and it is utilized in anabolism. [illegible] biochemical reactions are actually energy transfers
- During meta[illegible] are transformed from one form to the other by enzymes

- Enzymes act as **biocatalysts** and speed up and regulate metabolic pathways
- Enzymes are proteins that catalyze the speed up biochemical reactions. These are not changed during the reaction
- The molecules at which enzymes act are called **substrates**, and enzyme converts them into different molecules, called **products**.

Quick Quiz-3 (2) How does enzyme work?

HOW DOES ENZYME WORK?

- When enzyme attaches with substrate, a temporary enzyme-substrate (ES) complex is formed
- Enzyme catalyzes the reactions and substrate is transformed into product
- After it, the ES complex breaks enzyme product

$$E + S \rightarrow ES\ Complex \rightarrow E + P$$

(A) LOCK AND KEY MODEL

- In 1894, a German chemist Emil Fischer proposed lock and key model
- According to this model, both enzyme and substrate possess specific shapes that fit exactly into one another. This model explains enzyme specificity

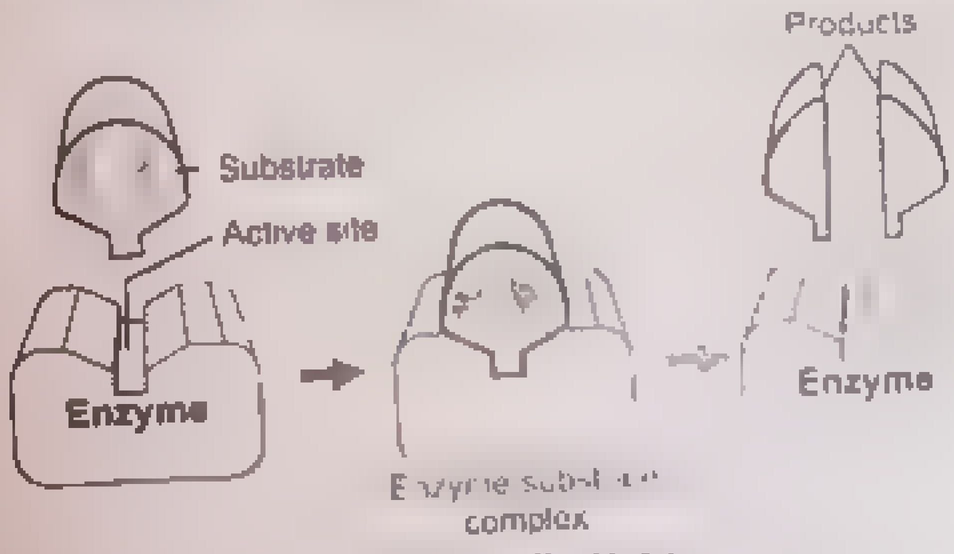
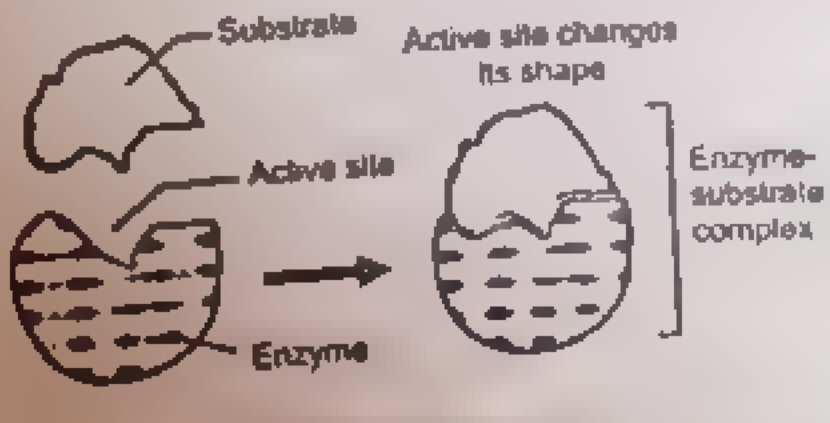


Fig. Lock and Key Model

(B) INDUCED-FIT MODEL

- In 1958, an American biologist **Daniel Koshland** suggested a modification to lock and key model and proposed **induced-fit model**
- According to this model, active site is not a rigid structure. Instead, it is molded into the required shape to perform its function



Induced Fit Model

"Induced fit model" is more acceptable than "lock and key" model of enzyme action

DO YOU KNOW?

(1) Wilhelm Kühne (1876) first time used the term enzyme.
(2) There are over 2000 known enzymes, each ... specific reaction
3) Enzymes are substrate ...
- The enzyme prot... by an enzyme amy...
- Similarly lipase enzyme acts ... digests them into fatty acids and glycerol

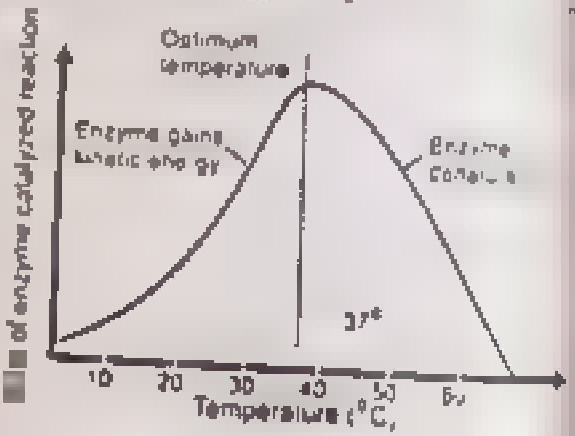
FACTORS AFFECTING ENZYME ACTIVITY

Exercise Q5 (iii) Briefly describe the factors that affect the Activity of enzymes

- Enzyme ...
- Any factor that can ... the chemistry or shape of enzyme molecule ... affect its activity

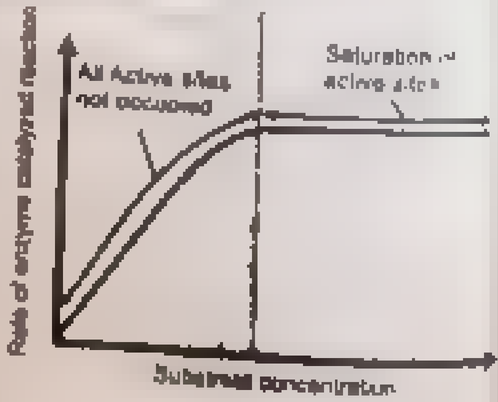
Following factors affect the enzyme activity

(i) TEMPERATURE



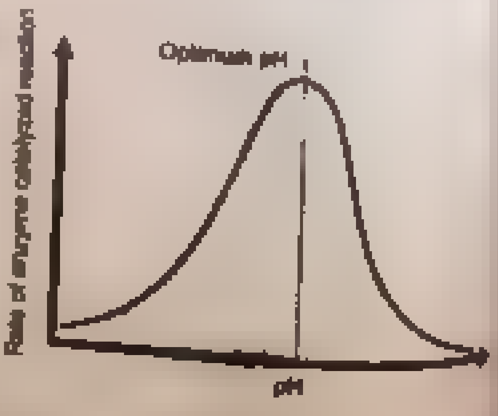
- Increase in temperature speeds up the rate of enzyme catalyzed reactions but only to a certain point
- Every enzyme works at its maximum rate at a specific temperature called as the optimum temperature for that enzyme
- When temperature rises to a certain limit heat adds in the activation energy and also provides kinetic energy for the reaction. So reactions are accelerated
- However when temperature is raised well above the optimum temperature, heat energy increases the vibrations of atoms of enzyme. Thus the globular structure of enzyme is lost. This is known as the denaturation of enzyme. It results in a rapid decrease in rate of enzyme action and it may be blocked completely

(ii) SUBSTRATE CONCENTRATION



- If enzyme molecules are available in a reaction then increase in substrate concentration increases the rate of reaction
- If enzyme concentration is kept constant and amount of substrate is increased then a point is reached where further increase in substrate concentration does not increase the rate of reaction.
  At this point the active sites of all enzymes are occupied at high substrate concentration.
  Thus more substrate molecules do not find free active site.
  This state is called saturation of active site and reaction rate does not increase

(iii) pH



- All enzymes work at their maximum rate at a narrow range of pH called as the optimum pH.
- A slight change in this pH causes retardation in enzyme Activity or blocks it completely
- Change in pH can affect the ionization of the amino acids at the active site
- Every enzyme has its specific optimum pH value
  e.g.
  pepsin (working in stomach) is active in acidic medium (low pH)
  trypsin (working in small intestine) shows its Activity in alkaline medium (high pH)

ROLE OF INHIBITORS IN ENZYME CATALYZED REACTIONS:

INHIBITORS

Substances that tend to decrease the activity of enzymes are called inhibitors

OR

An inhibitor is a chemical substance which can react (in place of substance) with the enzyme but is never transferred into products by blocking the active site of enzyme temporarily or permanently

Examples:

Poisons like cyanide, antibodies, anti metabolites [illegible]

TYPES OF INHIBITORS

Inhibitors can be divided into two types

(a) Irreversible inhibitors

(b) Reversible inhibitors

Irreversible Inhibitors

- They occupy the active sites by forming [illegible]
- They decrease the reaction rate by [illegible] enzymes

Reversible Inhibitors

- They form weak linkages with the enzyme
- Their effect can be neutralized completely or partly [illegible]

ROLE OF INHIBITORS

- The inhibitors may decrease the activity of enzymes and [illegible] either by combining directly with the enzyme or by reacting [illegible] remain available to enzyme for activation

There are two types of inhibitions

Competative Inhibition.

A number of inhibitors have structures similar to substrate molecules [illegible] substrate, they may be selected by the enzyme binding sites. However [illegible] site. They compete with the original substrate for the same binding site [illegible] higher than that of the substrate, so the substrate is displaced effectively [illegible] degree inactivated by the binding of the inhibitors. No products are [illegible] known as **"competitive inhibition"**

Example

Succinic acid (substrate) is converted into Fumaric acid (product) by [illegible]

Succinic dehydrogenase *(Enzyme)* + succinic acid *(Substrate)* → Fumaric acid + succinic [illegible]

But in the presence of malonic acid (competitive inhibitor) having [illegible] the binding sites are occupied by the malonic acid. Hence no [illegible] hence no product is formed

Succinic dehydrogenase *(Enzyme)* + Malonic acid *(Competitive inhibitor)* → No reaction possible *(Enzyme blocked)*

Non-Competative Inhibition

- ...
- Here ... distorts the enzyme structure also affecting ... genuine substrate binds the ...
- In the reactions catalysed by enzymes irreversible inhibitors cause irreversible inhibition ... blocking the active sites of enzymes or by occup... of reaction is retarded due to the occupation of active sites of enzymes by irreversible inhibitors ... destruction of the globular structure of enzymes

Note:
Competitive and non-competitive inhibitors are the ...

INDUSTRIAL APPLICATION OF ENZYME:

Enzymes are extensively used in different industries for fast chemical reactions. For exa...

(1) Food Industry: Enzymes that break starch into simple sugars are used ... buns etc

(2) Brewing Industry: Enzymes break starch and proteins. The products are used ... produce alcohol)

(3) Paper Industry: Enzymes break starch to lower its viscosity that aids in making pa...

(4) Biological detergent: Protease enzymes are used for the removal ... enzymes are used in dish washing to remove resistant starch resid...

QUICK QUIZ-3

(1) What are enzymes? Why are they called biocatalysts?

Enzymes are biocatalysts which alter the speed of metabolic activities in the living ...
Enzymes act as ***biocatalysts*** *because they speed up and regu...*

(2) How does enzyme work?

Page

(3) Who has used the term Enzyme first time?

Winhelm Kuhne (1978) first time used the term enzyme (Greek ...

(4) Why are following scientists famous for?

(i) Emil Fischer

In 1894, a German chemist, Emil Fischer proposed lock and key model to ... According to this model, both enzyme and substrate possess specific shapes ... This model explains enzyme specificity

(ii) Daniel Koshland

In 1958, an American biologist Daniel Koshland proposed the induced fit model ... According to this model, active site is not a rigid structure ... moulded into the ... perform its function

(5) Enzymes are extensively used in different industries. Comment on this statement.

Enzymes are extensively used in different industries for fast chemical reactions ...

(i) Food Industry: Enzymes that break starch into simple sugars are used ... buns etc

(ii) Brewing Industry: Enzymes break starch and proteins. The products are used ... produce alcohol

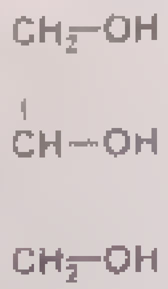
(iii) Paper Industry: Enzymes break starch to lower its viscosity that aids in making ...

(iv) Biological detergent: Protease enzymes are used for the removal ... enzymes are used in dish washing to remove resistant starch residues

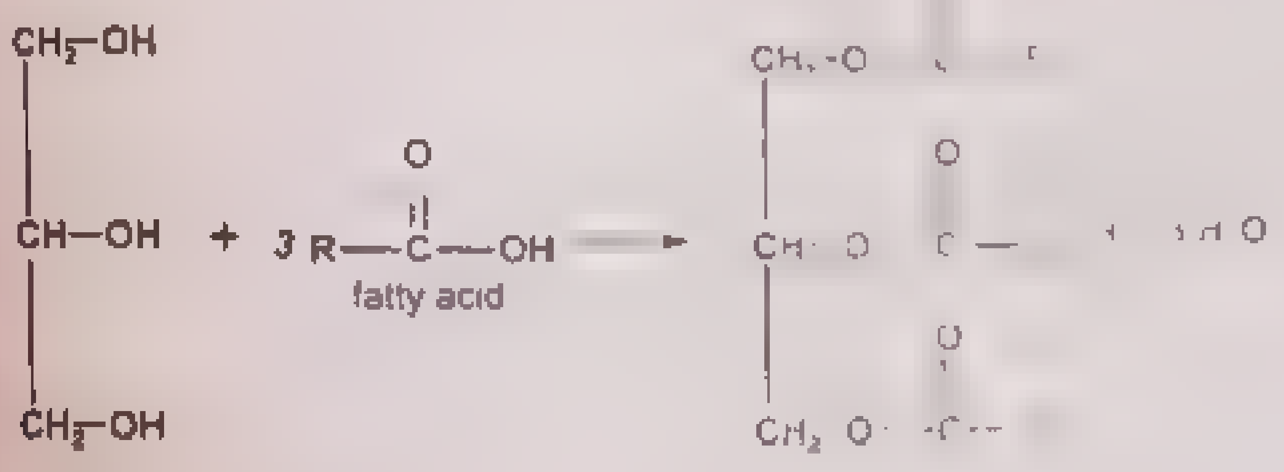
LIPIDS:

Naturally occurring organic compounds of animals and plants origin which are soluble in organic solvents called lipids

- The word lipid is derived from Greek word
- These molecules consist of carbon, hydrogen
- The main constituents of all membranes ... storage molecules intermediates in signaling pathways
- ***All lipids are hydrophobic:*** this is the one ... molecules includes fats and oils, waxes, phosp... and some other related compounds
- ***Fats and oils are made from two kinds of molecules*** ... with a hydroxyl group on each of its three carbon ... synthesis. Since there are three fatty acids attached



Glycerol



Glycerol fatty acid Triglyceride

CLASSIFICATION OF LIPIDS

There are three broad classes of lipids

SIMPLE LIPIDS

These are the ester of fatty acids with glycerol

Examples:

- ***Triglycerides, neutral fats:*** These are found in adipose tissue
- ***Waxes:*** beeswax, head oil of sperm whale, carnauba oil, and

COMPOUND LIPIDS

These contain radicals in addition to fatty acids and alcohols

Examples:

- ***Phospholipids (phosphatides):*** Found chiefly in animal tissues
- ***Plasmalogen:*** Found in brain, heart, and muscle
- ***Lipositol:*** Found in brain, heart, kidneys, and plant tissues together ... phosphatide linked to inositol, rapid synthesis and degradation processes.
- ***Sphingomyelin:*** Found in nervous tissue, brain, and red blood cells tissue

DERIVED LIPIDS

These are hydrolytic product of compound lipids.

Fatty acids: occur in plant and animal foods, also exhibit in complex ... from hydrolysis of fats, usually contains an even number of carbon a

Quick Quiz 4 3, Explain briefly the structure of lipids

STRUCTURE OF LIPIDS

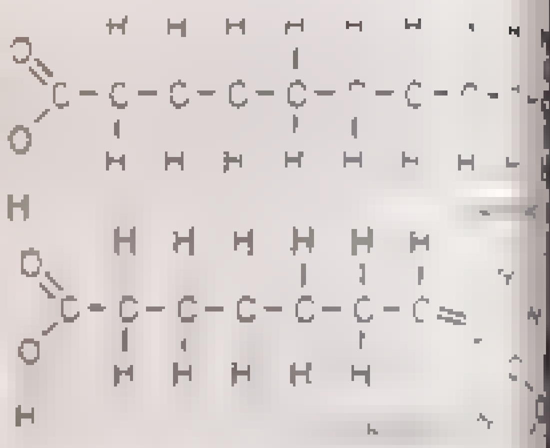
- Lipids are generally defined in terms of solubility a... proteins and nucleic acids are defined ...
- Lipids associate with ...

Structure of Fatty Acids

- The "tail" of a fatty acid is a ...
- The "head" of the molecule is a ...

Fatty acids are the main components of soap: ... in water to emulsify and wash away the oily dirt. However ... that whole molecule is hydrophob...

- The terms saturated mono-unsaturated and poly... shows the number of hydrogens attached to the ... of the fatty acids as compared to the number of d... between carbon atoms in the tail



FATS,

- Fats are mostly obtained from animal sources
- These have all single bonds between the carbons in their fatty acid tails. Thus all the carbons are also bonded to the maximum number of hydrogens possible. Thus these are called **saturated** fats
- ***Fats are solid at room temperature:*** It is because the hydrocarbon chains in these fatty acids are fairly straight and can ... closely ... points are high making these fats solid at room temperature

OILS:

- Oils are mostly obtained from plant sources. These have some double bonds between some ... in the hydrocarbon tail. It causes bends or "kinks" in the shape of the molecules
- Since, some of the carbon atoms share double bonds so they are bonded to less ... than saturated carbon atoms. Therefore these oils are called **unsaturated** fats
- ***Oils are liquid at room temperature:*** These are liquid at room temperature. It is because ... hydrocarbon tails, unsaturated fats cannot pack as closely together. Thus their melting p... making them liquid at room temperature

Important!
The unsaturated fats are "healthier" than the saturated ones

PROPERTIES OF LIPIDS

(1) PHYSICAL PROPERTIES

(1) Oils and fats may be either liquids or non crystalline solids at room temperature
(2) Fats and oils in the pure states are colorless, odorless and tasteless
(3) The color fats arise due foreign substances for example yellow color of the butter is due ... keratin
(4) They are lighter than water
(5) They are insoluble in water
(6) They are readily soluble in organic solvents like diethyl ether, carbon disulphide, acetone chloroform and carbon tetrachloride
(7) They form emulsions when they are agitated with water in the presence of soap or other emulsi...
(8) Fats and oils are poor conductor of heat and electricity and serve as excellent insulator for ...

(2) CHEMICAL PROPERTIES

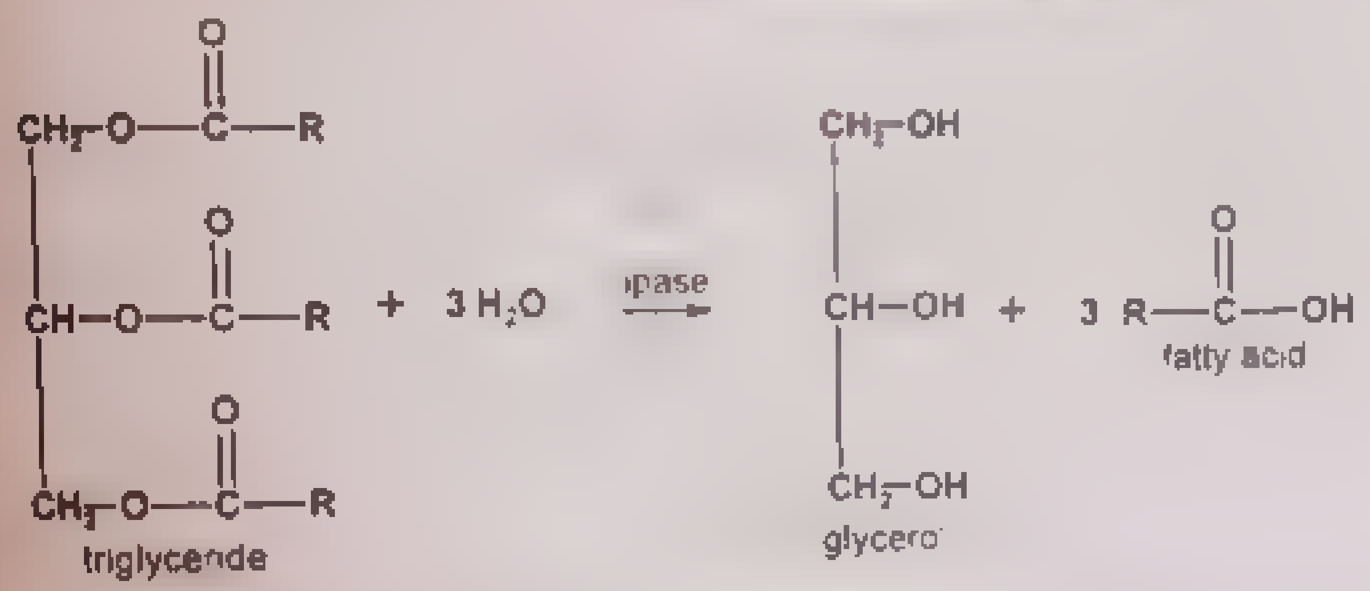
Fats and oils undergo various types of reaction but the most important are:

(i) Hydrolysis

(ii) Hydrogenation

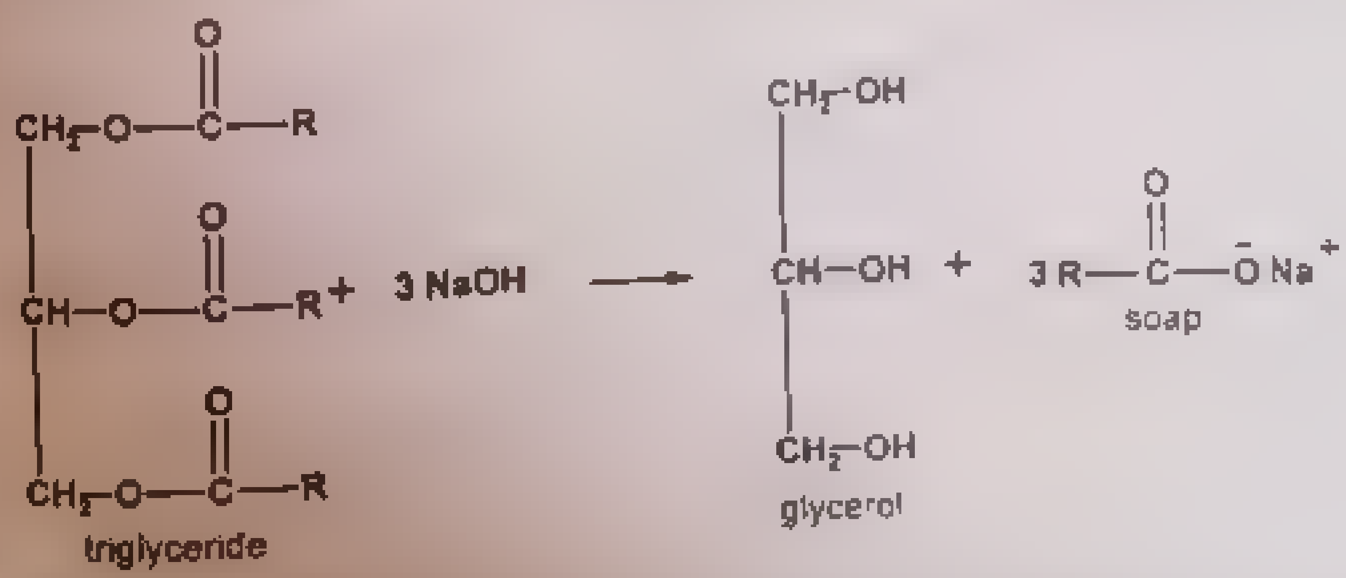
1. HYDROLYSIS OF FATS AND OILS

- Fats and oils are triglycerides. They are Triesters. They are hydrolyzed by enzymes which act as catalysts. These enzymes are called lipases.
- Actually, this hydrolysis takes place in the digestive tract of human beings and animals. Fatty acids are produced in animal body which play an important role in the metabolic pathways.



(2) SAPONIFICATION

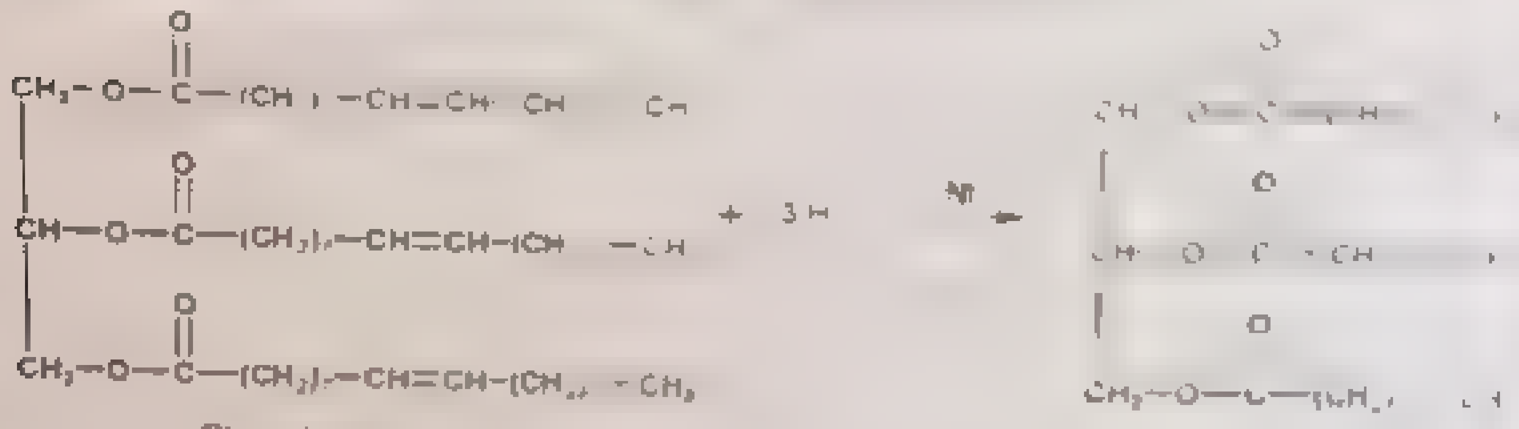
- Saponification is the hydrolysis of triglycerides by alkalies.
- Glycerol is produced along with sodium or potassium salt of fatty acids. These sodium and potassium salts are called soaps.



(3) HARDENING OF OILS

- The unsaturated triglycerides are liquids at room temperature. They are called oils.
- They can be saturated by passing hydrogen in them in the presence of metal catalysts. So, the triglycerides are converted into a semisolid triglyceride.

- This reaction is used commercially to harden the vegetable oil for the [illegible] margarine
- These harden [illegible]



Glyceryl linoleate (an oil) — Glyceryl stearate (a fat)

Exercise Q3 (iv). What is the nutritional importance of Lipids?

NUTRITIONAL IMPORTANCE OF LIPIDS

- Lipids play three major bioche[illegible]
  - (i) As a storage [illegible]
  - (ii) As components of mem[illegible]
  - (iii) As messengers (p[illegible]
- A major role of lipids in [illegible]
- Since unsaturated, saturated a[illegible] fats a[illegible] protein with 4 calories per g
- Even though [illegible] necessa[illegible] cause [illegible]
- Our body also needs fat from your diet to be able to absorb and use [illegible] vitamin A, vitamin D and vitamin E

ESSENTIAL LIPIDS

- Some nutrients are essential in diet for good health. These are not prepared in body.
- The essential lipids are polyunsaturated fats called omega 6 and omega-3 fats. These fats are [illegible] hormone synthesis, cell membrane structure and healthy brain and vision. They may help lower blood cholesterol levels
- The omega 6 fatty acids can be obtained from vegetable oils and nuts
- Omega-3 fatty acids are also in flaxseed, walnuts and fatty fish

NON-ESSENTIAL LIPIDS

- Monounsaturated fatty acids are not essential in the diet because our body can synthesize them
- They may help reduce risk for heart disease
- They are in olive oil, peanuts and avocadoes
- You do not need to get saturated fat, trans fat or cholesterol in your diet, and these lipids raise [illegible] cholesterol levels in your blood
- Saturated fat is in fatty meats and cheese, palm and coconut oil, and butter
- Trans fat is in partially hydrogenated oils in processed and fried foods, while cholesterol is [illegible] foods

Information

Our bodies make about 2 g of cholesterol per day, and that makes up about 85% of blood cholesterol, while [illegible] about 15% comes from dietary sources

FUNCTIONS OF LIPIDS

Some other functions of lipids are

- tissues reconstruction;
- nervous system organization;
- increases and assures a normal function of the skin;
- antibodies formation,
- good function of endocrine glands(thyroid)·
- water metabolism,

QUICK QUIZ-4

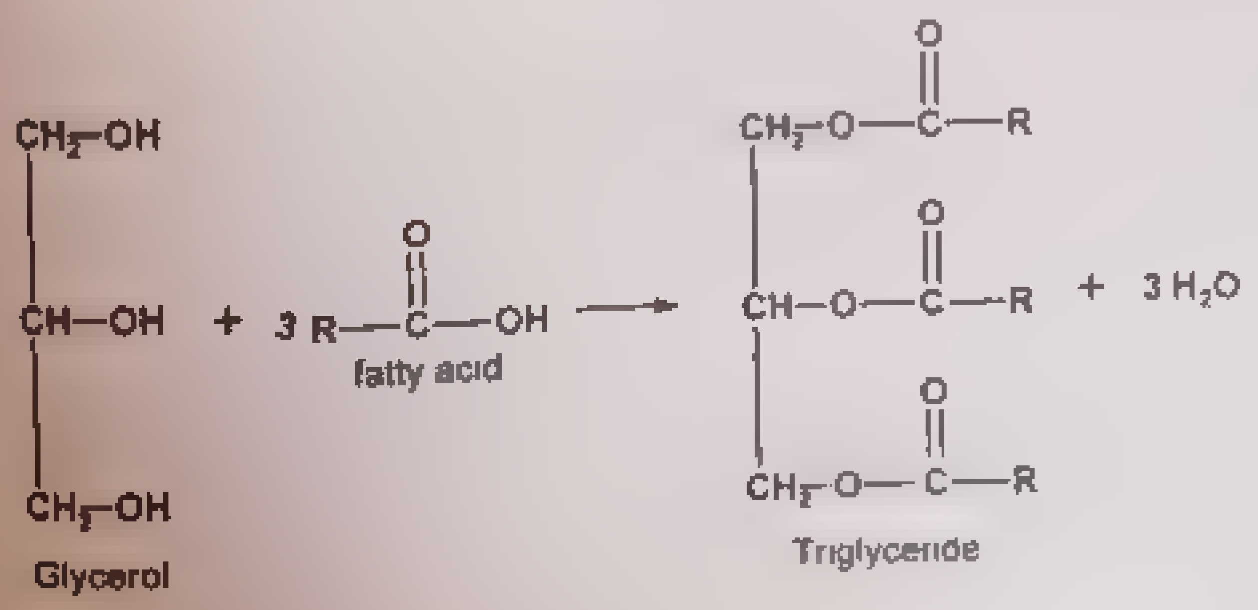
(i) *What are lipids? Shortly explain the only property that all the lipids have in common.*

Naturally occurring organic compounds of animals and plants origin which are soluble in organic solvents are called lipids.

All lipids are hydrophobic. This is the one property they have in common. This group of molecules includes fats and oils, waxes, phospholipids, steroids (like cholesterol) and some other related compounds.

(ii) *What are triglycerides? Draw its structure*

Fats and oils are made from two kinds of molecules: glycerol and three fatty acids joined by dehydration synthesis. Since there are three fatty acids attached, these are known as triglycerides.



(iii) *Explain briefly the structure of lipids.*

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NUCLEIC ACIDS

Discovery

(1) Nucleic acids were first of all demonstrated in the ...

(2) They were found in sperm heads by Friedrich M...

Nucleic acids are present in:

(1) In every living cell as well as in viruses

(2) They have been found to be essential substance of ge...

Properties

(1) Nucleic acids contain in their structures the blue-prints for the ... and every living organism

(2) They have two fundamental properties which are common to all living ...

a) The ability to reproduce, store and transmit genetic information

b) To undergo mutation

Types of Nucleic Acids:

There are two types of nucleic acids which have been discovered

(1) Deoxyribonucleic acids (DNA)

(2) Ribonucleic acid (RNA

Nucleic acids and proteins.

- In the human body the nucleic acids ... as part of the conjugated ... nucleoproteins
- The nucleic acids direct the synthesis of proteins

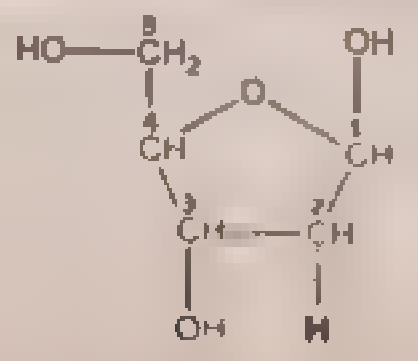
Exercise Q3 iv. Explain the structures of Nucleic acids

STRUCTURAL COMPONENTS OF DNA AND RNA

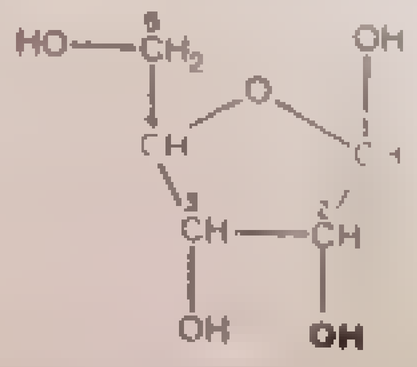
- DNA stands for deoxyribonucleic acid. It is a polymer of deoxyribonucleotides
- RNA stands for ribonucleic acid. It is a polymer of ribonucleotides
- The nucleotide consists of one sugar, one nitrogenous base and ...
- The structures of all components are given below

(i) SUGAR

- The sugar in DNA is deoxyribose
- The sugar in RNA is ribose
- The deoxy prefix indicates that this form of the sugar contains ... oxygen atom. The pentose sugar has two hydrogens attached to it instead of a hydrogen and hydroxyl (-OH)



Deoxyribose sugar



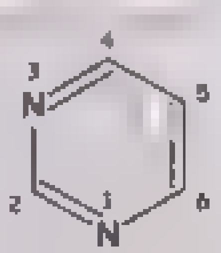
Ribose

- All of the nitrogenous bases are linked to the C ... atom of ...
- The phosphate group is attached to the ... OH group ...

...) NITROGENOUS BASES

...ck Quiz-5 (2) *Differentiate purines and pyrimidines.*

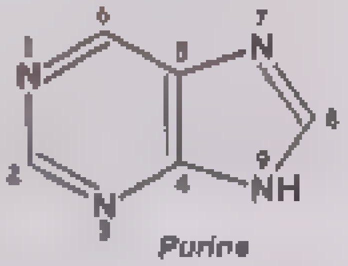
...) Pyrimidines



Pyrimidine

- There are three pyrimidine bases.
- Each consists of a 6-membered ring containing both nitrogen and carbon atoms
- Two pyrimidines Thymine and Cytosine are found in DNA
- RNA also contains two pyrimidines but they are Cytosine and Uracil

...) Purines



Purine

- The purines are made from two heterocyclic rings of carbon and nitrogen
- In purines a 6-member and a 5-member ring are fused.
- There are two purines, Adenine and Guanine.
- These are found in both DNA and RNA.

...) PHOSPHATES

- The addition of one or more phosphate groups to a nucleoside makes it a nucleotide
- The nucleotide consists of a base-sugar-phosphate unit
- These units on polymerization forms DNA

...erence between DNA and RNA

...y differ in following ways.

...) The sugar in RNA is ribose while the sugar in DNA is 2-deoxyribose
...) Four different bases are found in DNA cytosine (C), thymine (T), adenine (A) and guanine (G)
In RNA thymine does not occur and its place is taken by uracil (U).
...) DNA is nearly always double stranded, while RNA is usually single strand
...) DNA is used to store information while RNA is used to transfer information

...UICK QUIZ-5

...) ***Write the names of structural components of DNA and RNA***

Both DNA and RNA are polymers of nucleotides

The nucleotide consists of one sugar, one nitrogenous base and at least one phosphate

Sugar:	In DNA, it is deoxyribose sugar and in RNA it is ribose sugar
Nitrogen bases:	In DNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Thymine
	In RNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Uracil
Phosphate.	The phosphate is similar in both DNA and RNA

...) ***Differentiate purines and pyrimidines***

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...) ***Which purines are present both in DNA and RNA?***

Two purines are present in both DNA and RNA. Adenine (A) and ...

MINERALS OF BIOLOGICAL SIGNIFICANCE

- [illegible]
- [illegible]
- [illegible] ations in food
- [illegible] is mineral matter, vital to all mental & physical [illegible]
- They are most important [illegible] processes, are constituents of the bones, tissues, blood [illegible]
- Many of them act as cata[illegible] in the human body
- [illegible] through the nervous system, digestion [illegible] utilization of all nutrients in foods
- Vitamins cannot be properly assimilated without the correct balance of minerals. e.g. calcium [illegible] vitamin "C" utilization, zinc for vitamin "A", magnesium for "B" complex vitamins, selenium [illegible] absorption etc.

Important minerals in human diet and their roles

Minerals	Role in body	
Major minerals		
Sodium	Fluid balance in the body. Helps in absorption of other nutrients	
Potassium	Fluid balance in the body. Acts as cofactor for enzymes	Important for muscle con[illegible]
Chloride	Fluid balance in the body. Component of hydrochloric acid	
Calcium	Development and maintenance of bones and teeth and Blood clotting	
Magnesium & Phosphorus	Development and maintenance of bones and teeth	
Trace Minerals		
Iron	Oxygen transport and storage	
Zinc	Aids insulin action. Helps in growth and reproduction	Act as en[illegible] Sup[illegible]
Copper	Acts as enzyme cofactor	
Chromium	Helps in insulin action	
Fluoride	Stabilizes bone mineral and hardens tooth enamel	
Iodine	Essential for normal thyroid function	

SOURCES OF IMPORTANT MINERALS

Exercise Q3 (a) *Describe four important minerals and their sources.*

CALCIUM

Calcium is important to bone growth and formation, blood clotting and nerve and muscle functioning.

Sources:

Calcium is obtained from milk, cheese, egg yolk, beans, nuts, cabbage etc.

Deficiency:

A deficiency may result in arm and leg muscles spasm & softening of bones, back and leg cramps, brittle bones, rickets, poor growth, osteoporosis, tooth decay and mental depression.

IRON

- Iron is an essential mineral.
- Its major function is to combine with protein and copper in making hemoglobin. The hemoglobin is present in the blood and carries oxygen from the lungs to the tissues throughout the body.

Sources:

Iron is obtained from red meat, egg yolk, whole wheat, fish, spinach and mustard etc.

Deficiency:

A deficiency may result in weakness, fatigue, paleness of the skin, constipation and anemia.

PHOSPHORUS

- Phosphorus is after calcium the second most abundant mineral in the body.
- It is a principal mineral of bones and teeth.
- It is involved in most metabolic actions in the body, including [illegible] growth and contraction of the heart muscle.

Sources: Phosphorus is obtained from egg yolk, cheese, milk, cabbage etc.

Deficiency: A deficiency is unusual but may have symptoms varying from [illegible] fatigue, anxiety, numbness, skin sensitivity and changes in body weight.

ZINC

- Zinc is vital to immune resistance, wound healing, digestion, [illegible] taste and smell and maintaining normal Vitamin A levels and usage.
- Zinc can be found in almost every cell of the body and serves as [illegible] body processes.

Sources: We get zinc from Oyster, red meat, chicken, beans, nuts, [illegible]

Deficiency: A deficiency may result in poor growth, acne-like rash, hair loss, diarrhea, delayed sexual maturation, impotence, sterility, eye lesions, loss of appetite, reduced sense [illegible] poor wound healing, reduced resistance to infections, mental [illegible] nails and anemia.

BIOLOGICAL SIGNIFICANCE OF MINERALS

(A) IMPORTANCE SIGNIFICANCE OF IRON

The primary role of iron relates to the ab[illegible] oxygen [illegible]

Some functions of iron are mentioned here [illegible]

Fatigue

- To prevent fatigue, iron is needed by the body to make he[illegible] the cells
- It is also needed for adenosine triphosphate production [illegible] proper cell function

Exercise

- Iron is lost through sweat and through [illegible]
- Studies indicate that 34% of female runners and 8% [illegible]

Pregnancy

- Iron is needed for proper placenta development
- It is also needed for the [illegible]
- Studies estimate that up to [illegible]

Pediatric

- Iron is essential during the first eight mo[illegible]
- The effects of anemia may be associated with developme[illegible] delays in both motor and cognitive [illegible]

Treatment Duration

- Up to six months to restore low iron stores, its sufficient quantity [illegible]
- When iron deficiency is left untreated, it can lead to conditions [illegible]

Metabolic Processes

- Iron plays an important part in the metabolic processes of the an[illegible]
- The function of iron in the body is limited almost exclusi[illegible] hemoglobin
- It is present in some enzymes that catalyze reactions of [illegible]
- In human body, the richest organs in iron are liver [illegible]
- In smaller amount, it is also present in bones, med[illegible]

(B) IMPORTANCE SIGNIFICANCE OF CALCIUM

Occurrence in Human

- Calcium is the most common mineral in the human body
- It is present in the body in almost the same relative abundance as in the [illegible]
- There are six stable isotopes of calcium, calcium40 is the most [illegible] abundant (0.003 %).

Importance

- The integrity of the system depends critically on vitamin D status. If there is a def[illegible] its calcaemic action leads to a decrease in the ionised calcium and sec[illegible] hypophosphataemia. This is why experimental vitamin D deficiency results in [illegible] calcium deficiency gives rise to osteoporosis
- Approximately 99% of total body calcium is in the skeleton and teeth and 1 [illegible]
- Calcium has four major biological functions
  - (i) Structural as stores in the skeleton
  - (ii) Electrophysiological - carries charge during an action potential across [illegible]
  - (iii) Intracellular regulator, and

(iv) As a ...

IMPORTANCE SIGNIFICANCE OF PHOSPHORUS

Occurrence in Human

- Phosphorus is present ...
- There is over 1 ...
- is a constituent of ...
- It is found in complex ...
- The calcium phosphate is ...
- Phosphorus compounds are ... phosphate are added to foods ...

Importance

(i) The main function of ...
(ii) It plays an important ... protein for the growth, ...
(iii) It is also crucial for the ...
(iv) Phosphorus works with ...
(v) It also assists in the contraction ... the heartbeat and in nerve ...

IMPORTANCE SIGNIFICANCE OF ZINC

- Zinc is the most omnipresent of a ...
- More than a hundred specific ...
- If zinc is removed from the ...
- Studies in individuals with a ... These include impairments of ...
- Acrodermatitis enteropathica ...
- Loss of zinc through gastro... body
- Considerable amount of ... reabsorbed and this process ...
- Other routes of zinc excretion ...

SOCIETY, TECHNOLOGY AND SCIENCE

Glycogen – A store house

Glycogen is reserved food material that store ... energy due to lack of glucose, the glycogen reconverts ... ATP

Hibernating Animals and Reserve Food

Large amount of fat is store in the boy of so... activities slow down. They use this fat as reserved food ...

COMPLEX CARBOHYDRATES WHICH PROVIDE LUBRICATION TO THE ELBOW AND KNEE.

- Glucosamine, glucosaminoglycans or proteoglycan ... lubrication to elbow and knee
- Glucosamine ($C_6H_{13}NO_5$) is an amino sugar ... building cartilage and lubricating joints ... procurer for glycosaminoglycans and for glycosylated ...
- Glucosamine has been shown to help keep our joints ... connective tissue. It is a naturally occurring nutrient ... group and a sugar molecule (glucose)

- Over time even da[illegible] damaged [illegible]
- [illegible] damaged [illegible]

GLUCOSAMINOGLYCANS (GAGs)

These are the [illegible] containing a repeating disa[illegible] GalNAc. GAGs have negative [illegible]

- **Chondroitin sulphate** D g[illegible] Keratan sulphate Gal + GlcN[illegible]
- **GAGs** have unique propert[illegible] molecules. Because of high viscosity [illegible] joints especially in knee and elbow. On the [illegible]
- **Proteoglycans** (mucoportiens) are formed of gly[illegible] bonded to each other. These are found in all connective tissues.
- **Proteoglycans** can also be called joint grease. Proteoglycan appears to be a necessary [illegible] synovial fluid for normal joint lubrication and function. (Synovia[illegible] function of which is to serve as a lubricant in joints or tendon shea[illegible]
- **Aggrecan** is one of the most important extra cellular proteoglycan. To each aggrecan's core [illegible] chains of chondroitin sulphate and keratin sulphate are covalently attached through the [illegible] They play an important role in hydration of cartilage of joints. They give cartilage its ge[illegible] lubricate it and provide resistance to deformation.

FIBROUS PROTEINS FROM HAIR AND SILK

- Fibrous proteins consist of elongated molecules having one or more polypeptide chains in the [illegible]
- Secondary structure is most important in them.
- They are insoluble in aqueous media, a property due to a high concentration of hydrophobic a[illegible] residues both in interior of the proteins and or its surface.
- They are non-crystalline and are elastic in nature.
- Their characteristic feature is regular repeating pattern.
- They play structural or supporting role in the body.

Examples: are silk fiber, keratin (of nails and hair), myosin (in muscle cells), fibrin of blood clot.

INSULIN – A PROTEIN HORMONE WHOSE DEFICIENCY LEADS TO DIABETES MELLITUS

Structure:

- Insulin is a 51 amino acid peptide hormone that is produced exclusively by pancreatic beta cells.
- F. Sanger was the first scientist who determined the sequence of amino acids in insulin.
- After 10 years of careful work, he concluded that insulin is composed up of 51 amino acids in two cha[illegible] one alpha chain and one beta chain.
- The alpha chain contains 21 amino acids.
- The beta chain contains 30 amino acids. Both chains are held together by disulphide bridges. T[illegible]
- The molecule weight of insulin is 5808.

Function.

- Insulin hormone is central in regulating carbohydrate and fat metabolism in the body.
- It causes the cells in liver, muscles and fat tissue to take up glucose from the blood.
- In the liver and skeletal muscles glucose is stored as glycogen, while in adipocytes it is stored as triglycerides.
- Insulin stops the use of fat as energy source. When blood glucose level falls below a certain limit the body begins to use stored sugar as an energy source through glycogenolysis.
- As a central metabolic control mechanism, its status is also used as a control signal to other body systems (such as amino acids uptake by body cells).
- In addition, it has several other anabolic effects throughout the body.
- Insulin is used medicinally to treat some forms of diabetes patients.

ROLE OF MINERALS IN THE BODY

- Minerals act as cofactors for the enzyme reactions. Enzymes ... All cells require enzymes to work and function. They give us our vitality.
- They maintain the pH balance with in the body.
- Minerals actually facilitate the transfer of nutrients across cell membranes.
- They maintain proper nerve conduction.
- Minerals help to contract and relax muscles.
- They help to regulate our bodies' tissue growth.
- Minerals provide structural support for the body.

These are two categories of mineral essential with in body, macro-minerals and micro-minerals. There is no one mineral deficiency. They all must be maintained in balance within body.

MACRO-MINERALS

- Calcium
- Chloride
- Phosphorous
- Sodium
- Potassium
- Sulfur
- Magnesium

MICRO-MINERALS (OR TRACE MINERALS)

- Iron
- Boron
- Chromium
- Iodine
- Manganese
- Molybdenum
- Selenium
- Silicon
- Copper
- Cobalt
- Rubidium
- Germanium
- Lithium
- Zinc
- Vanadium

[illegible]

CALCIUM

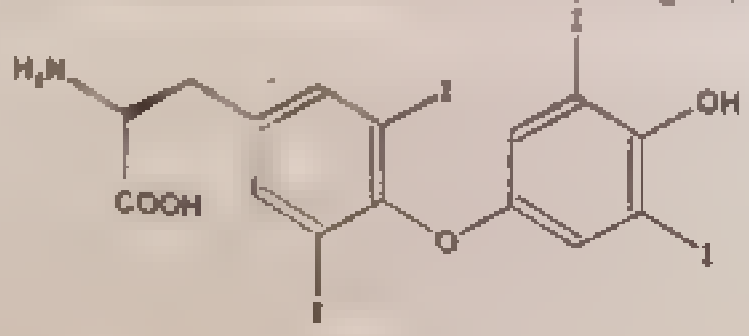
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]

FLUORINE

- [illegible]
- [illegible]
- [illegible]
- [illegible] teeth and bones causing fluorosis
- [illegible] during high fluorine intake [illegible] irregularly distributed chalky patches on the surface of the enamel which become stained yellow or brown producing a characteristics mottled appearance

IODINE

- [illegible] thyroid hormones, thyroxine and triiodothyronine
- [illegible] of the iodine absorbed is trapped by the thyroid gland

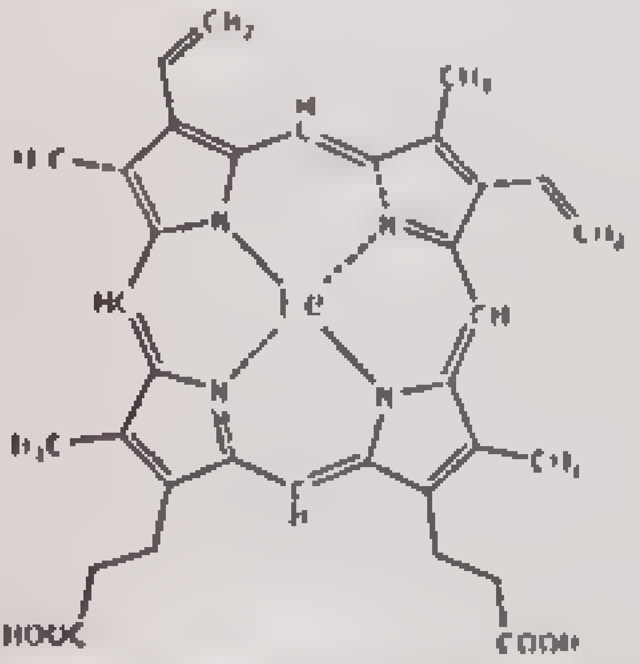


Thyroxine

- **Most environmental iodine occurs in seawater**
- People living far from the sea are at particular risk of deficiency
- Salt fortified with iodide typically 70ug/g, helps ensure adequate intake 100ug/day
- Deficiency is rare in areas where iodized salt is used but common world wide
- Iodine deficiency develops when iodide intake is less than 20ug/day
- In mild or moderate deficiency the thyroid gland hypertrophies to concentrate iodine in itself resulting goitre which is an enlargement of the thyroid gland visible as a swelling of front the of neck
- **Excessive** iodine consumption can lead to thyrotoxicosis a condition resulting from high concentrations of thyroid hormones in the body which can result from eating foods that have high amounts of iodine such as kombu type kelp or seaweed

[IR]ON

- Iron (Fe) is a component of hemoglobin, myoglobin, and many enzymes in the bod.
- Heme iron, contained mainly in animal products is absorbed much better than non heme iron, which accounts for over 85% of iron in the average diet.
- However, absorption of nonheme iron is increased when it is consumed with animal protein and vitamin C.
- The Recommended Daily Allowance (RDA) of iron is 8 milligrams for men and postmenopausal women.
- Iron deficiency, which may be caused by improper vegan or ovo-lacto vegetarian diets.
- Chronic bleeding may also cause iron deficiency. Iron may accumulate in the body when a person is given repeated blood transfusions or takes an overdose of iron supplements.
- Excess iron is toxic any damage the intestines and other organs, as well as cause vomiting and diarrhea.



Heme, a constituent of hemoglobin

[M]AGNESIUM

- Magnesium (Mg) has several important metabolic functions in the production and transport of energy.
- It is also important for the contraction and relaxation of muscles.
- Magnesium is involved in the synthesis of protein, and it assists in the functioning of some enzymes.
- Most dietary magnesium comes from nuts, cereals, and dark green, leafy vegetable which are rich in chlorophyll.

[M]ANGANESE

- Manganese (Mn) is necessary for healthy bone structure and is a component of several enzyme systems including manganese-specific glycosyltransferases and phosphoenolpyruvate carboxykinase.
- Manganese is found in cereal and nuts.
- The adequate intake of manganese is 2 to 5 mg/day.

[M]OLYBDENUM

- Molybdenum (Mo) is a component of coenzymes necessary for the activity of xanthine oxidase, sulfite oxidase, and aldehyde oxidase.
- Sulfite oxidase catalyses the transformation of sulfite to sulfate which is necessary for metabolism of sulfur containing amino acids, such as cysteine.
- Legumes such lentils, beans, and peas are good sources of molybdenum.

POTASSIUM

- Potassium (K) ... in response to excess sodium intake.
- The adequate intake of potassium ... for older person.
- Potassium is generally ...
- Potassium from supplements ... is consumed by individuals with chronic ...

SELENIUM

- Selenium (Se) is a part of the enzyme ... from polyunsaturated fatty acids.
- Selenium is also a part of they enzyme that ...
- Generally, selenium acts as an antioxidant that works with ...
- The deficiency of selenium causes Keshan disease ...
- The RDA for selenium is 70 micrograms (mcg).
- The tolerable upper level of selenium is 400 mcg/day for adults based on ... brittleness and early signs of chronic selenium toxicity.

SODIUM

- Sodium (Na) is usually consumed as table salt, Sodium Chloride (NaCl).
- The adequate intake of 1.5 grams per day with an upper limit of 2.3 grams per day ... needs for sweat losses for individuals 8 years or older engaged in recommended levels of physical ...
- Active people in humid climates who sweat excessively may need more than the adequate intake.

ZINC

- Zinc (Zn) is contained mainly in bones, teeth, hair, skin, hair, liver, muscle, leukocytes and ...
- Zinc is a component of several hundrd enzymes, including many nicotinamide adenine ... (NADH) dehydrogenases, RNA and DNA polymerases, and DNA tanscription factors as ... phosphatase, super oxide dismutaise and carbonic anhydrase.
- Good dietary sources of zinc include mollusks, such as oysters and cereals.

KEY POINTS

- Carbohydrates are the most abundant macromolecule on earth. They are of three types i.e. Mono..., disaccharides and polysaccharides.
- People eating a diet high in carbohydrates are less likely to accumulate body fat compared with those who ... carbohydrate/high fat diet.
- Proteins are the most important class of biomolecules. They are major structural components of animals and human tissues. They are classified as a simple a protein, conjugated proteins and derived proteins. They are actually polymers of Amino acids.
- Nucleoproteins act as the carrier of heredity from one generation to the other.
- Hemoglobin is a protein and carrier of oxygen. Some of the proteins act as hormones.
- Enzymes are biocatalyst and catalyze chemical reactions in living organisms. They are quite specific in their function. Their Activity depends upon temperature, substrate concentration and pH. They are protein in nature and are used extensively in food, brewing, paper industries.
- All lipids are hydrophobic. Fats are solid while oils are liquid at room temperature. They are insoluble in water but soluble in organic solvents such as diethyl ether, acetone, benzene etc.
- Some lipids are essential for our diet and some are non-essential.
- Nucleic acids are present in every living cell as well as in viruses. They have ability to reproduce, store and transfer genetic information. They are of two types DNA and RNA. Nucleotide is the structural unit of DNA and consists of ... sugar, one nitrogenous base and at least one phosphate.
- Minerals are the nutrients and are as necessary as oxygen for life. They are constituents of teeth, bones, tissues, ... muscles and nerve tissues.
- Minerals are classified as major and trace minerals i.e. those required in appreciable quantity are major and those required in low quantity are trace.

EXERCISE

1. Select the right answer from the choices given with each question.

(i) Biochemistry covers the practical applications of:
(a) Medicine (b) Agriculture (c) Nutrition (d) All of these

(ii) Macromolecules are of how many types?
(a) Three (b) Four (c) Five (d) Six

(iii) The general formula for Carbohydrates is:
(a) $N_n(H_2O)_n$ (b) $P_n(H_2O)_n$ (c) $C_x(H_2O)_y$ (d) [illegible]

(iv) Most organic matter on earth is made up of:
(a) Carbohydrates (b) Lipids (c) Oligosaccharides (d) Proteins

(v) The no. of Carbon atoms in Hexose is:
(a) One (b) Four (c) Six (d) Ten

(vi) The long chains of Amino Acids are called:
(a) Oils (b) Polypeptides (c) Proteins (d) Monopeptides

(vii) Proteins are used in both forms of:
(a) Catabolism (b) Anabolism (c) Enzymes (d) Metabolism

(viii) What is TRUE about enzymes?
(a) They make biochemical reaction to proceed spontaneously
(b) They lower the activation energy of a reaction
(c) They are not very specific in their choice of substrates
(d) They are needed in large quantities

(ix) To what category of molecules do enzymes belong?
(a) Carbohydrates (b) Lipids (c) Nucleic acids (d) Proteins

(x) What is TRUE about cofactors?
(a) Break hydrogen bonds in proteins (b) Help facilitate enzyme Activity
(c) Increase activation energy (d) Are composed of proteins

(xi) Prosthetic groups are:
(a) Required by all enzyme (b) Loosely attached with enzymes
(c) Proteinsous nature (d) Tightly bound to enzymes

(xii) Lipids are generally defined in terms of:
(a) Solubility (b) Structure (c) Molarity (d) All of these

(xiii) DNA and RNA are made up of:
(a) Peptides (b) Nucleotides (c) Neutrons (d) None of these

(xiv) ______ of the human body weight is mineral matter?
(a) 5 % (b) 10 % (c) 50 % (d) 100

(xv) ______ is needed for Vitamin C utilization.
(a) Acid (b) Iron (c) Phosphorus (d) Calcium

(xvi) The component of blood that carries oxygen in the body is:
(a) Fats (b) Myoglobin (c) Hemoglobin (d) Amino Acids

(xvii) Most RNA molecules are:
(a) independent (b) Double Stranded (c) Single Stranded (d) Multiple Stranded

(xviii) ______ are the major component of soap.
(a) Fatty Acids (b) Palm Oils (c) Proteins (d) [illegible]

(xix) The mineral, related with the formation of bones and teeth, is:
(a) RNA (b) Phosphorus (c) Iron (d) Sulphur

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d) All of these	**(ii) Ans: (b) Four**
Biochemistry covers medicine, agriculture, nutrition etc.	Four main types [illegible] They are carbohydrates [illegible]
(iii) Ans: (c) $C_x(H_2O)_y$	**(iv) Ans: (a) Carbohydrates**
The general formula for carbohydrates is $C_x(H_2O)_y$. That's why	Most organic matter [illegible]

such ... carbohydrates e.g. ...	
(v) Ans: (c) Six ... e.g.	**(vi) Ans: (b) Polypeptides**
(vii) Ans: (d) Metabolism Metabolism ...	**(viii) Ans: (b) They lower the activation energy of reaction**
(ix) Ans: (d) Proteins ...	**(x) Ans: (b) Help facilitate enzyme Activity**
(xi) Ans: (a) Required by all enzymes Prosthetic group is ... work. ... are required	**(xii) Ans: (a) Solubility**
(xiii) Ans: (b) Nucleotides DNA and RNA are polymers ... consists of: one sugar, one ... phosphate	**(xiv) Ans: (a) 5 %**
(xv) Ans: (d) Calcium Calcium is needed ...	**(xvi) Ans: (c) Hemoglobin**
(xvii) Ans: (c) Single Stranded RNA molecules are ... double stranded	**(xviii) Ans: (a) Fatty Acids**
(xvii) Ans: (b) Phosphorus The main function ... phosphorus ... formation ... and teeth. The ... phosphate is the principal ... bones and teeth	

Q2: Give brief answers for the following questions.

(i) What do you understand by the word Biochemistry?

Biochemistry is the branch of science concerned with studying the various molecules that occur and organisms with their chemical reactions.

Biology is the science of living organisms and chemistry is the science of atoms and biochemistry is the science of the atoms and molecules in living organisms.

(ii) Briefly state the functions of Carbohydrates

The main functions of carbohydrates are given below.

- These are source of energy.
- These are necessary for proper fat metabolism.
- These are the only source of energy for the brain and nerve tissues.
- Some carbohydrates support the growth of healthy bacteria in the intestines for digestion.
- Some carbohydrates high in fibre helps prevent constipation and lowers the risk for cancer, heart disease and diabetes.
- They are storehouse of energy, e.g. starch is the food stores in plants and glycogen in animals.
- They build the structure of plants and animals as cellulose or pectin.

Name the classes and sub-classes of Proteins

Proteins are classified into three types

(A) Simple Proteins.	**e.g.** Albumins Globulins Glutelins Histones Scleroproteins
(B) Conjugated proteins	**e.g.** Nucleoproteins Mucoprotein Glycoprotein Phosphoprotein
(C) Derived proteins	**e.g** Proteans Proteases [illegible]

In a range of 0-35°C the rate of reaction of an enzyme is proportional to temperature. Justify it

- When temperature rises to 35°C [illegible] for the reaction. So reactions are a [illegible]
- However, when temperature is raised well above [illegible] cases the vibrations of atoms of enzyme. Thus, the globular structure of enzyme is [illegible] a rapid dec [illegible] ate of enzyme action

How does pH affect enzyme Activity?

- All enzymes work at their [illegible]
- Change in pH can affect the [illegible]
- Every enzyme has its spe [illegible]
  e.g. pepsin (working in stomach) is active in acidic medium low pH

Describe lock and key mechanism of enzyme action

In 1894, a German chemist, Emil Fischer proposed lock and key mode

According to this model [illegible]

This model explains enzyme [illegible] only

e.g. lipase enzyme acts [illegible] cannot act on proteins

What is the main use of enzymes in paper industry?

Enzymes break starch to lower its viscosity that aids in making paper

Define cofactor and co-enzymes.

The non-protein part of enzyme is called co-factor or co-enzyme

Without cofactor enzyme cannot [illegible]

- Co-factors include inorga [illegible] metalic molecules
- Fe^{2+} ions are cofactor for chrome oxidase enzyme, etc
- Nicotinamide adenine dinuc [illegible]

Shortly explain the only property that all the Lipids have in common

Naturally occurring organic compounds [illegible] solvents are called lipids.

All lipids are hydrophobic. This is the one property they have in common. This group of molecules includes fats and oils, waxes, phospholipids, steroids (like cholesterol) and some other related compounds

Explain the structural components of DNA and RNA

Both DNA and RNA are polymers of nucleotides

The nucleotide consists of one sugar, one nitrogenous base, and at least one phosphate

Sugar:	In DNA, it is deoxyribose sugar and in RNA it is ribose sugar
Nitrogen bases:	In DNA four nitrogenous bases are Adenine, [illegible]
	In RNA, four nitrogenous bases are [illegible]
Phosphate.	The phosphate is similar in both DNA and RNA

(xi) Define Lipids and state the difference between fat and oil

Naturally occurring orga[illegible] called lipids. They are water [illegible]

Fats	Oils
(1) They are [illegible]	1 [illegible]
(2) They are saturated	2 [illegible]
(3) They are [illegible] semi [illegible]	3 [illegible]
(4) They possess high [illegible]	4 [illegible]
(5) They have [illegible] of saturation	5 [illegible]

(xii) Briefly state how Vitamin D is formed in human body?

When ultraviolet light falls upon 7 [illegible] erted into vitamin D. This [illegible] present naturally in the [illegible] extent, this mater[illegible]

(xiii) State the differences between the chemical structures of DNA and RNA

They differ in following ways

- The sugar in RNA is ribose while the sugar in DNA is 2 deoxyribose
- Four different bases are found in DNA cytosine (c) thiamine (T), adenine (A) and guanine (G). In RNA thiamine does not occur and its place is taken by uracil [illegible]
- DNA is nearly always double stranded while RNA is [illegible]
- DNA is used to store information while RNA is used to transfer information

(xiv) Briefly state why minerals are important for human life

- They are constituents of the teeth, bones, tissues, blood, muscle and nerve cells
- Many of them act as catalysts for many biological reactions within the human body
- They are necessary for transmission of messages through the nervous system, digestion, & metabolism
- Vitamins cannot be properly assimilated without the correct balance of minerals. e.g. calcium is needed for vitamin "C" utilization etc

(xv) Name different routes for the loss of Zinc from human body.

- Loss of zinc through gastrointestinal tract accounts for approximately half of all zinc eliminated from the body
- Considerable amount of zinc is secreted through the biliary and intestinal secretions but most of it is reabsorbed
- Other routes of zinc excretion include the urine and surface losses (desquamated skin, hair, sweat

Q3: Give detailed answers for the following questions.

(i) Describe different classes of Carbohydrates.
Page 388

(ii) Explain the structure of Proteins.
Page 396

(iii) Briefly describe the factors that affect the Activity of enzymes.
Page 400

(iv) What is the nutritional importance of Lipids?
Page 406

(v) Explain the structures of Nucleic acids.
Page 409

(vi) Describe four important minerals and their sources.
Page 412

YOUR SKILLS

Marks: 85

OBJECTIVE

30 Minutes **Marks: 17**

Over writing, cutting, erasing, using lead pencil will result in loss of marks

Circle the correct option i.e. A/B/C/D. Each part carries one mark.

(i) Carbohydrates are .... Compounds

(a) carbonyl (b) polyhydroxy

(ii) Which of the following is not a carbohydrate

(a) ribose (b) glucose (c) mannose (d) formaldehyde

(iii) What is general formula of carbohydrates

(a) $Cn(H_2O)_{n+1}$ (b) $C_n(HO)_n$ (c) $C_nH_nO_n$

(iv) Which one of the following carbohydrates does not

(a) ribose (b) glucose (c) galactose (d) None

(v) Which carbohydrate is present in grapes

(a) glucose (b) fructose

(vi) Which of the following is present in milk?

(a) galactose (b) lactose

(vii) One glucose molecule combine with galactose

(a) sucrose (b) starch (d) lactose

(viii) Which one of the following is a polysaccharide

(a) cellulose (b) starch (c) both a & b

(ix) 1 gram of fat contains approximately

(a) 4 k cal (b) 9 cal (c) 9 k cal

(x) Macromolecules are of how many types?

(a) 3 (b) 4 (c) 5

(xi) Prosthetic groups are

(a) Required by all enzymes ... tightly bound to enzyme

(xii) Lipids are generally defined in terms of

(a) solubility (b) structure (c) Molarity (d) all of these

(xiii) Minerals constitute ... human body weight

(a) 10 % (b) 100 % (c) 5 % (d) 50 %

(xiv) .... is part of enzyme glutathione peroxides

(a) Zn (b) Se (c) Mn

(xv) In adults .... of iodide absorbed is trapped by thyroid gland

(a) 50 % (b) 70 % (c) 80 % (d) 100 %

(xvi) Which one of the following is considered ... mineral for body

(a) iron (b) iodine (c) calcium (d) both a & c

(xvii) Calcium has .... stable isotopes

(a) 7 (b) 9 (c) 6 (d) 11

SUBJECTIVE

Time: 2:35 Hours **Total Marks Section B and C: 68**

Section - B (Marks 42) 14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

(i) (a) Define carbohydrates (1)

(b) All organic compounds which have general formula $C_x(H_2O)n$ are not carbohydrates. Justify (2)

(ii) Describe role of carbohydrates in living organisms (3)

(iii) (a) Define monosaccarides. (1)

(b) What are source of monosaccarides (2)

(iv) (a) How monosaccarides are classified? (2)

(b) What are polysacarides (1)

(v) (a) Define disaccarides (1)

(b) What are sources of disaccarides (2)

(vi) (a) Define glycosidic linkage with example (1)

(b) What is glycemic index. (2)

(vii) (a) Compare glycogen in starch. (1)

(b) Draw structure of Amylose. (1.5)

(viii) (a) What is chitin (1.5)

(b) What is source of children. (1)

(ix) (a) What are bacterial polysaccarides?

(b) What is role of bacterial polysaccaride in living organisms? (2)
(xi) (a) What are globulins. (2)
(b) What is source of Gluten? (1)
(xii) What are conjugated Proteins. (3)
(xiii) How quaternary structure of protein is formed? (3)
(xiv) (a) What is haemoglobin. (1)
(b) Differentiate between Anabolism & Catabolism. (2)
(xv) (a) Describe Lock and Key model. (2)
(b) What are enzymes. (1)
(xvi) (a) How does Induce – Fit Model describe mechanism of enzyme Action (1.5)
(b) Enzymes are specific in their action. Justify. (1.5)
(xvii) (a) What is optimum temperature for enzyme? (1)
(b) How does temperature affect enzymatic activity. (2)
(xviii) (a) What are inhibitors? (1)
(b) Describe types of inhibitors. (2)
(xviii) (a) What is spring myelin? (1)
(b) What are fatty acids? (2)
(xix) (a) What is saponification. (1.5)
(b) What is meant by hardening of oil. (1.5)

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

Q3. (a) Discuss functions of Polysaccharides. (5)
(b) Describe the structure of Proteins. (4)
(c) How enzymes work as biocatalyst. (4)
Q4. (a) Classify Proteins. (5)
(b) What are the factors which affect enzymatic activity (4)
(c) How inhibitors decrease the enzymatic activity (4)
Q5. (a) Explain the structure of Lipids. (5)
(b) Differentiate between DNA & RNA. (4)
(c) What is role of minerals in our body? (4)

CHAPTER # 22
INDUSTRIAL CHEMISTRY

INTRODUCTION:

Definition:

The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity is called Industrial Chemistry.

Development of Industrial Chemistry

- The scientists thought how [illegible] laboratory scale. This thinking started the development of [illegible]
- Chemistry knowledge was applied [illegible] recipes". These recipes are now called chemical processes.
- Industrial chemistry keeps up with the progress in science and [illegible] incorporates other emerging disciplines such as biotechnology, microelectronics, pharmacology, and [illegible]
- It is also concerned with economics and the need to [illegible]

The link between Classical and Industrial Chemistry

- The Classical Chemistry (organic, inorganic and physical chemistry) is very essential for advancing the science of chemistry. It discovers and and report new products [illegible] and techniques.
- The Industrial Chemistry helps us to close the gap between classical chemistry as it is taught in colleges and universities, and chemistry as it is practiced commercially.

Scope of Industrial Chemistry

- The scope of industrial chemistry therefore includes
  - ✓ The use of materials and energy in appropriate scale
  - ✓ Application of science and technology to enable [illegible] experiences the benefits of chemistry in different areas: *food production, health and hygiene* [illegible] *and entertainment.*

INTRODUCTION TO THE CHEMICAL INDUSTRY

The chemical industry can also be classified according to the type of [illegible] materials used and [illegible] principal products made.

(1) Industrial inorganic chemical industries

Industrial inorganic chemical Industries extract inorganic chemical substances, make composites of them [illegible] and also synthesize inorganic chemicals.

(2) Industrial organic chemical industries.

- Heavy industrial organic chemical industries produce petroleum fuels, polymers, [illegible] other synthetic materials, mostly from petroleum.
- Light organic industries produce specialty chemicals which include pharmaceuticals, [illegible] paints, pesticides, soaps and detergents, cosmetic products and miscellaneous [illegible]

THE STRUCTURE OF THE GLOBAL CHEMICAL INDUSTRY

- Normally a value is given to something according to its im[illegible]
- Some things are of high value while others are of [illegible]
- The low valued products are needed to produce in large [illegible] to make significant profit. This means that the raw materials are cheap and easily accessible. There is also an existing, relatively simple and easily accessible processing technology.
- To sell a large volume of product, there must be a large [illegible]. This brings stiff competition [illegible] makes the price to remain low.

COMMODITY CHEMICALS:

Commodity chemicals are defined as low-valued products produced in large quantities mostly in continuous processes. They are of technical or general purpose grade.

- The global chemical industry is founded on basic inorganic chemicals (BIC) and basic organic chemicals (BOC) and their intermediates. It is because they are produced directly from [illegible] sources or immediate derivatives of natural resources. They are produced in large quantities.
- Some of the top ten BIC are sulphuric acid, nitrogen, oxygen, ammonia, [illegible] sodium hydroxide, phosphoric acid and chlorine. The sulphuric acid is always number one. It is because it is used in the manufacture of fertilizers, polymers, drugs, paints, detergents and paper. It is also used in [illegible] refining, metallurgy and in many other processes. The top ranking of oxygen is due to its use in [illegible] industry.
- Among top ten BOC are Ethylene and propylene. They are used in the production of [illegible] chemicals including polymers.
- BIC and BOC are referred to as commodity or industrial chemicals.

SPECIALTY CHEMICALS:

High-value adding involves the production of small quantities of chemical products for specific end uses. Such products are called specialty chemicals.

- These are high value-added products produced in low volumes and sold on the basis of a specific function.

Example:

Performance chemicals. These are high value products produced in low volumes and used in extremely low quantities. They are judged by performance and efficiency. Enzymes and dyes are performance chemicals.

Other Examples:

medicinal chemicals, agrochemicals, pigments, flavour and fragrances, personal care products, surfactants and adhesives.

- Specialty chemicals are mainly used in the form of formulations.
- Purity is of vital importance in their formulation. Thus highly valued pure chemicals must be prepared known as fine chemicals.

FINE CHEMICALS:

They are high value-added pure organic chemical substances produced in relatively low volumes and sold on the basis of exact specifications of purity rather than functional characteristics.

The raw materials for a product need to be very pure for the product to function as desired.

Examples:

Research chemicals, pharmaceutical ingredients, etc.

The global market share for each type is roughly as follows:

Commodities = 80% **Specialties Chemicals = 18%** **Fine Chemicals = 2%**

Exercise Q3 (i) What is chemical industry? Discuss different raw materials used in this industry.

The chemical industry comprises the companies that produce industrial chemicals

RAW MATERIAL FOR THE CHEMICAL INDUSTRY

- All chemicals are derived from raw materials available in nature
- The price of chemicals depends on the availability of their raw materials
- Major chemical industries have therefore developed around the most plentiful raw materials
- The natural environment is the source of raw materials for the chemical industry

RAW MATERIALS FROM THE ATMOSPHERE

- The atmosphere is the field above ground level
- It is the source of air from which six industrial gases N_2, O_2, Ne, Ar, Kr and Xe are manufactured
- The mass of the earth's atmosphere is approximately 5×10 [illegible] tons. Therefore the supply of the gases is almost unlimited

RAW MATERIALS FROM THE HYDROSPHERE

- Ocean water is about 1.5×10^{21} litres.
- It contains about 3.5 percent by mass dissolved material
- Seawater is a good source of sodium chloride, magnesium and bromine

RAW MATERIALS FROM THE LITHOSPHERE

- The vast majority of elements are obtained from the earth's crust in the form of mineral ores, carbon and hydrocarbons.
- Coal, natural gas and crude petroleum are used as energy sources. These are also converted to thousands of chemicals.

RAW MATERIALS FROM THE BIOSPHERE

- Vegetation and animals contribute raw materials to the so-called agro-based industries
- Oils, fats, waxes, resins, sugar, natural fibres and leather are examples of thousands of natural products

QUICK QUIZ-1:

(1) Name those disciplines which play important role in industrial chemistry

The industrial chemistry has a strong link with the Classical Chemistry which includes organic, inorganic and physical chemistry. The classical chemistry discovers and report new products, routes and techniques which are then used in industrial chemistry. The industrial chemistry also includes disciplines such as biotechnology, microelectronics, pharmacology and material science

(2) Define Industrial chemistry

The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity is called Industrial Chemistry.

(3) What is difference between organic and inorganic chemical industries?

- The organic chemical industry is based upon compounds of carbon. These may be [illegible] origin or may be synthetic e.g. polymers, petrochemicals, dyes, paints, pesticides, soaps etc.
- The inorganic chemical industries are largely based upon compounds of elements [illegible] extract inorganic chemical substances, make composites of the same and [illegible] chemicals

5. [illegible] atmosphere

6. In which [illegible] materials are present

7. Give few natural products

8. Give examples of Basic organic chemicals

9. What do you mean by commodity chemicals

10) What is meant by performance chemicals

These are high value pro[illegible]
judged by performance and ef[illegible]

11) Give share of different types of chemicals in global market

The global market share for each type is [illegible]
Commodities 80% [illegible] Chemicals [illegible]

SAFETY CONSIDERATIONS IN PROCESS INDUSTRIES

INTRODUCTION

[illegible] e.g. During the 1980s [illegible] to prevent major accidents. The process safety management [illegible] associations initiated programmes to develop and provide process safety management guide[illegible] members. For example these associations are in the United State[illegible] the Centre for Chemical Proce[illegible] (CCPS), the American Petroleum Institute (API) and the Chemical Manufacturers' Association (CMA

PROCESS SAFETY MANAGEMENT REQUIREMENTS

- Process safety management is an integral part of the overall chemical processing facility safety programme
- An effective process safety management programme requires the leadership, support and involvement of top management, facility management, supervisors, employees, contractors and [illegible]

ELEMENTS OF THE PROCESS SAFETY MANAGEMENT PROGRAMME

There are a number of basic requirements which should be included in every chemical process safety management programme

(1) Process Safety Information

- Process safety information is used by the process [illegible] to define critical processes materials and equipment
- It includes all available written information about process technology, process equipment, raw materials and products. It also includes the information about chemical hazards before conducting a process hazard analysis.
- Other critical process safety information is documentation rel[illegible] project reviews and design basis criteria

(2) Employee Involvement

- Process safety management programmes [illegible] participation in the development and conduct of process safety analyses and [illegible]
- Access to process safety information [illegible] process hazard analyses is usually provided to all employees and contractor employees [illegible] area
- Most industrialized nations require that workers be [illegible] instructed in the identification, nature and safe-handling of all chemicals to which they may be exposed

(3) Process Hazard Analysis

- After the process safety information is compiled a thorough process hazard analysis is carried out
- It includes systematic multi-disciplinary process hazard analysis appropriate to the complexity of the process.
- It is conducted in order to identify, evaluate and control the hazards of the process
- Persons performing the process hazard analysis should be knowledgeable and experienced in relevant chemistry, engineering and process operations
- Each analysis team normally includes at least one person who is thoroughly familiar with the process being analysed and one person who is competent in the hazard analysis methodology being used

(4) Management of Change

- Chemical process facilities should develop and implement programmes which provide for the revision of process safety information procedures and practices as changes occur
- Such programmes include a system of management authorization and written documentation for changes to materials, chemicals, technology, equipment, procedures, personnel and facilities that affect each process.

(5) Operating Procedures

- Chemical processing facilities must develop and provide operating instructions and detailed procedures to workers.
- Operating instructions should be regularly reviewed for completeness and accuracy (and updated or amended as changes occur) and cover the process unit's operating limits

(6) Safe Work Practices

- Chemical process facilities should implement hot work and safe work permit and work order programmes to control work conducted in or near process areas
- Supervisors, employees and contractor personnel must be familiar with the requirements of the various permit programmes. These include permit issuance and expiration and appropriate safety, materials handling and fire protection and prevention measures.

(7) Employee Information and training

- Chemical process facilities should use formal process safety training programmes [illegible] and [illegible] reassigned and new supervisors and workers.
- The training provided for chemical process operating and maintenance supervisors [illegible] be comprehensive

QUICK QUIZ-2:

(1) *What are requirement of process safety management*

An effective pr...

2) *How employees should be involved in safety management programme*

- ...
- ...

3) *What is analysis te...*

Each analysis te... analysed and one person w...

(4) *What is role of man... of change in process industries?*

- Chemical pr... process saf...
- Such prog... materials ...

Exercise Q3 (II). What are dyes? How are they classified on the basis of structure?

DYES

A dye is a coloured compound ... used in solution which is capable of being fixed to a fabric

The dye ... exposure to sunlight ... that the ... soap ...

- The dye color is due to the presence of a chromophore
- Its fixing ... is due to ... basic auxochromic groups such as OH, SO_3H, NH_2, ...
- The polar auxochrome makes the ... water-soluble and binds the dye to the fabric by ... the oppositely charged groups of the fabric structure.

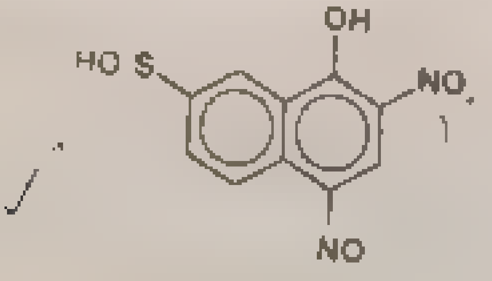
CLASSIFICATION OF DYES BY STRUCTURE

Dyes are classified according to the type of chromophores present in their structures. This method of classification includes the following main types.

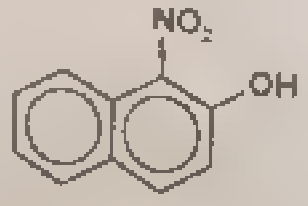
(1) NITRO AND NITROSO DYES:

The NO_2 and NO groups are chromophores in this class of dyes.

Examples:



Naphthalene Yellow S



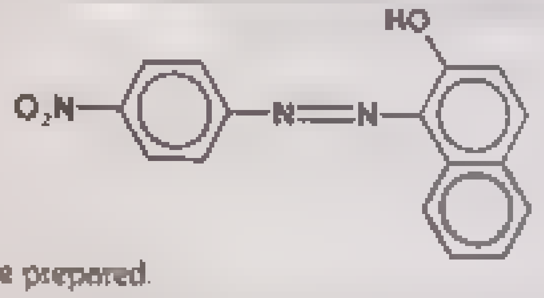
Mordant Green 4

AZO DYES:

- The azo dyes contain one or more azo groups, -N=N- as the primary chromophore
- The common auxochromes are NH_2, NR_2, OH, SO_3H etc
- Azo dyes form the largest and most important group of synthetic group of synthetic dyes. They are highly colored
- They can be prepared by diazotising an aromatic amine to produced diazonium salt. It is then coupled to a compound series. Thus, azo dyes can be produced with almost any color

Examples

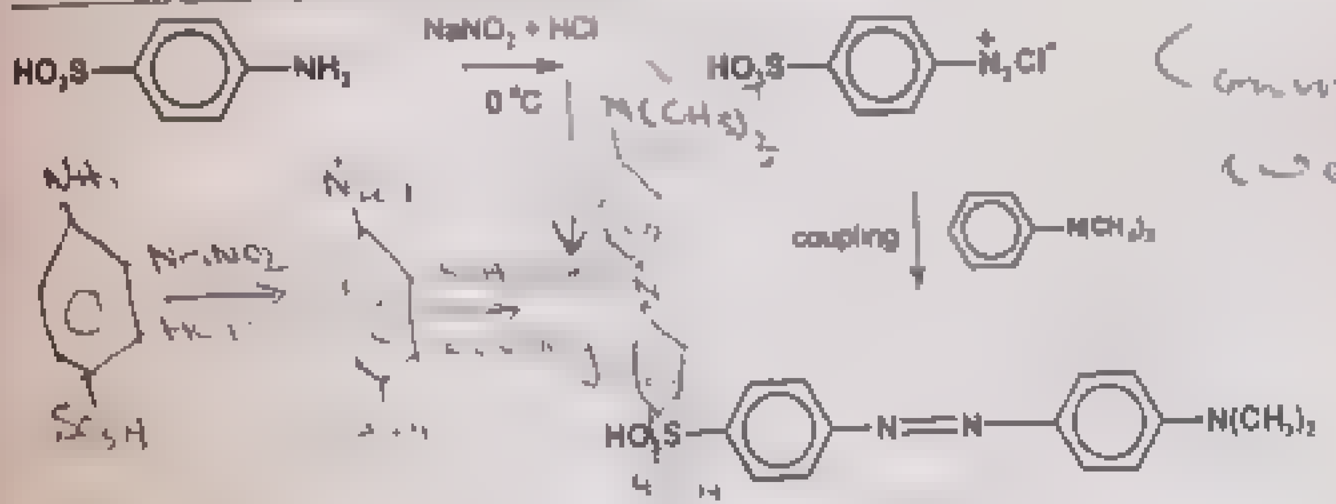
(a) Para Red



- It was the first azo dye to be prepared.
- Para red is obtained by the reaction of diazotized p-nitroaniline with β-naphthol on fabric itself

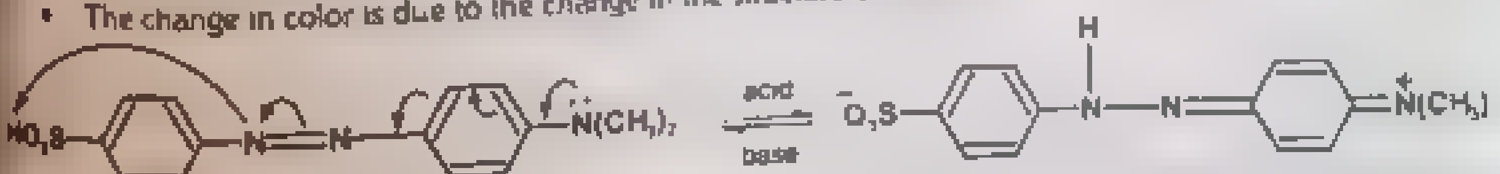
(b) Methyl Orange.

- Methyl orange is obtained from sulphanilic acid by the following steps

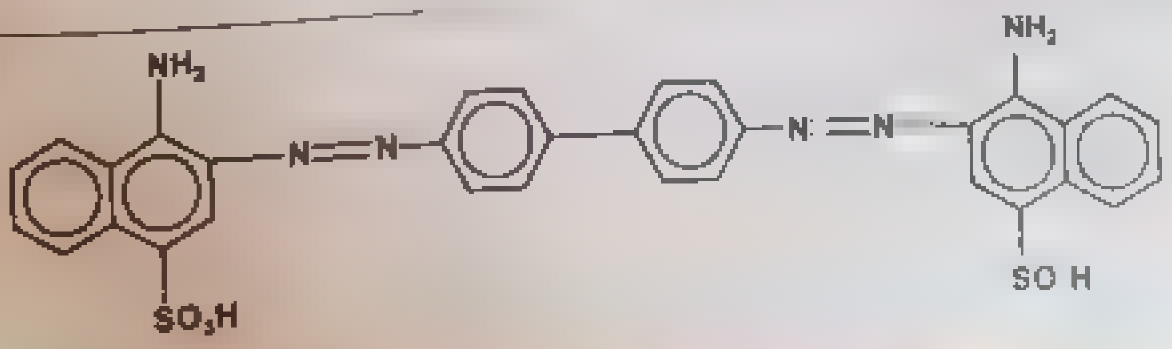


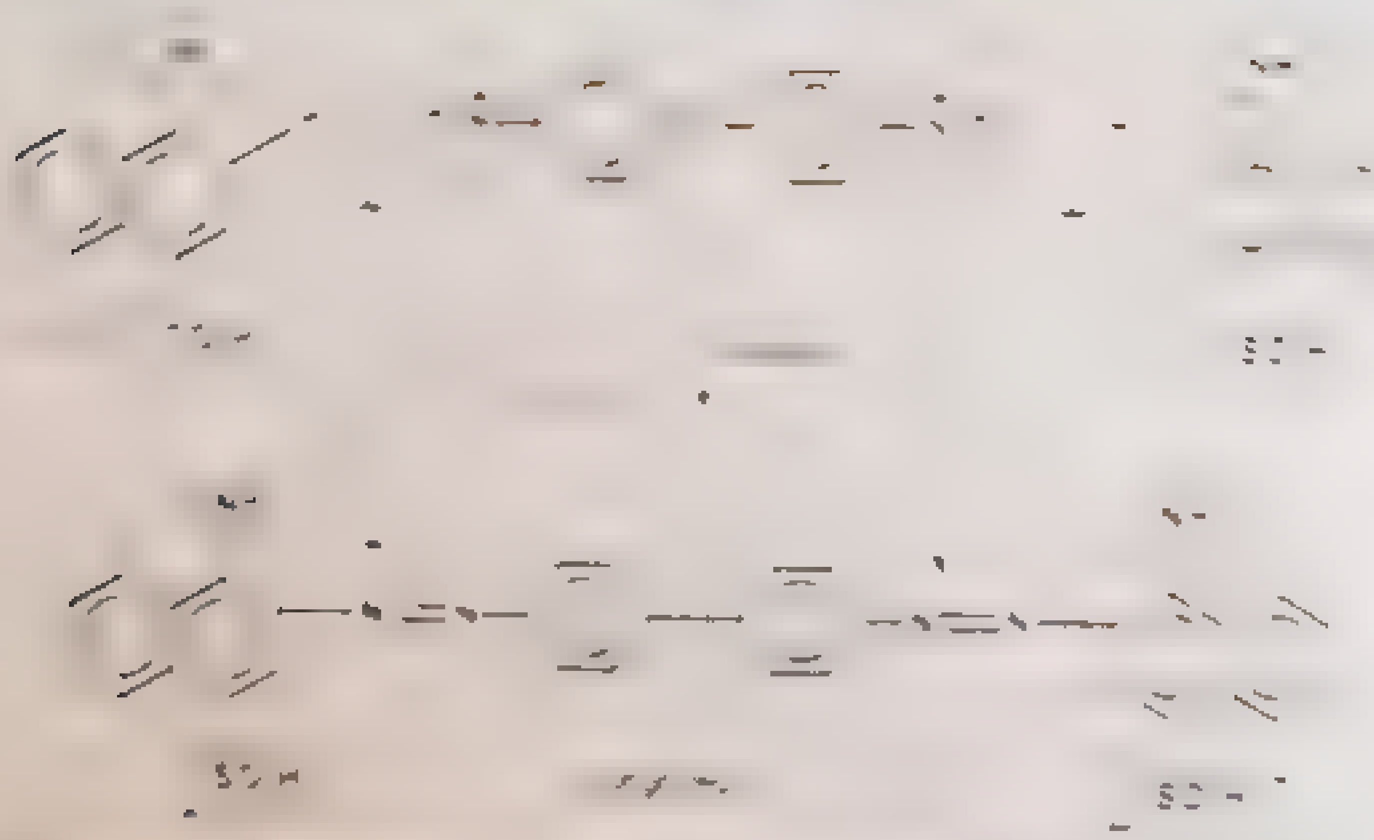
methyl orange

- Methyl orange imparts orange color to wool and silk.
- However, the color is not fast to sunlight or washing
- It is a valuable indicator for acid base titrations because it gives yellow color in basic solution and red color in acid solution.
- The change in color is due to the change in the structure of the ions

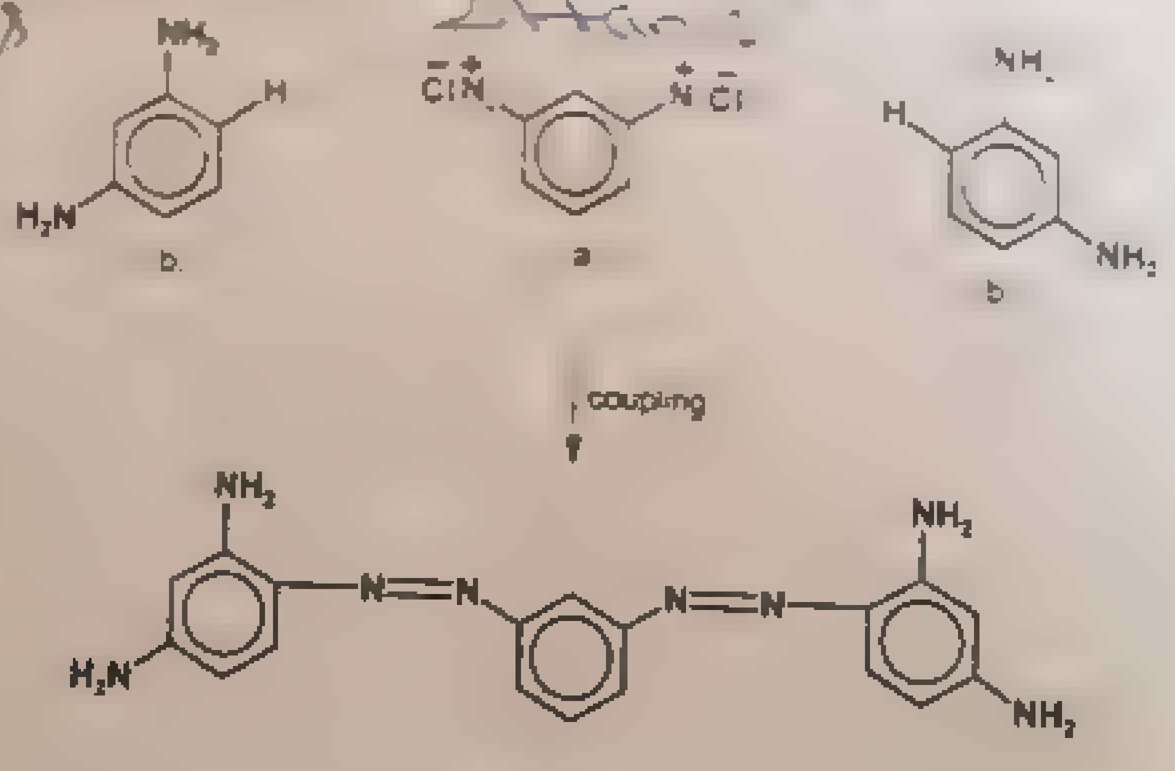


(c) Congo Red





(4) Bismarck Brown

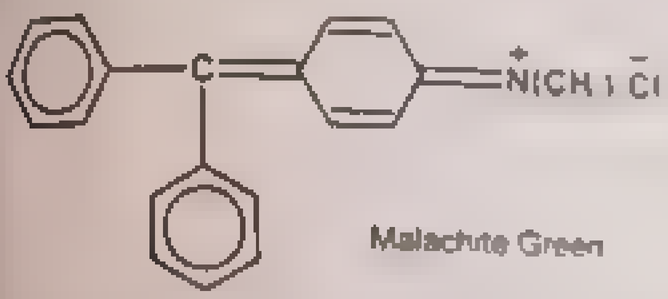


Bismarck Brown

TRIARYLMETHANE DYES:

- In triarylmethane dyes, a central carbon is bonded to three aromat... form (the chromophore)
- The auxochromes are $-NH_2$, $-NR_2$ and $-OH$. Examp...

Malachite Green:

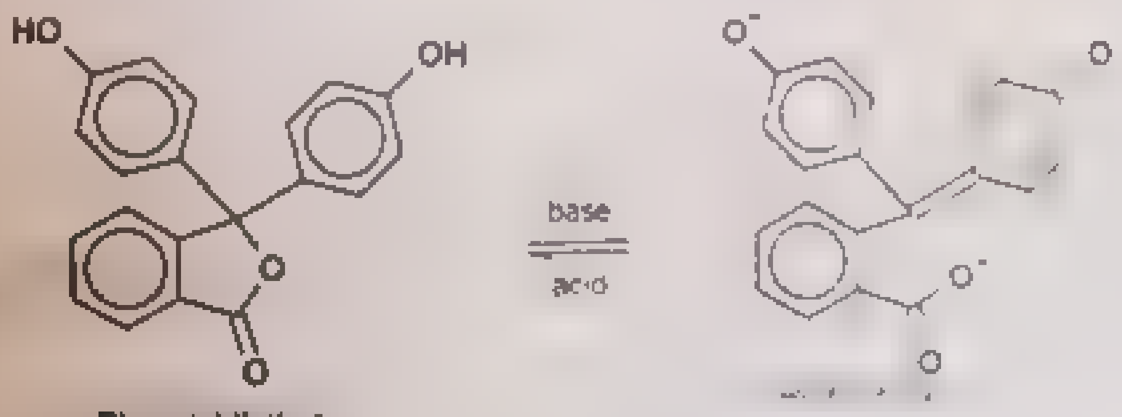


Malachite Green

- Malachite green has a deep green-blue c...
- Although the color fades in light, malach...

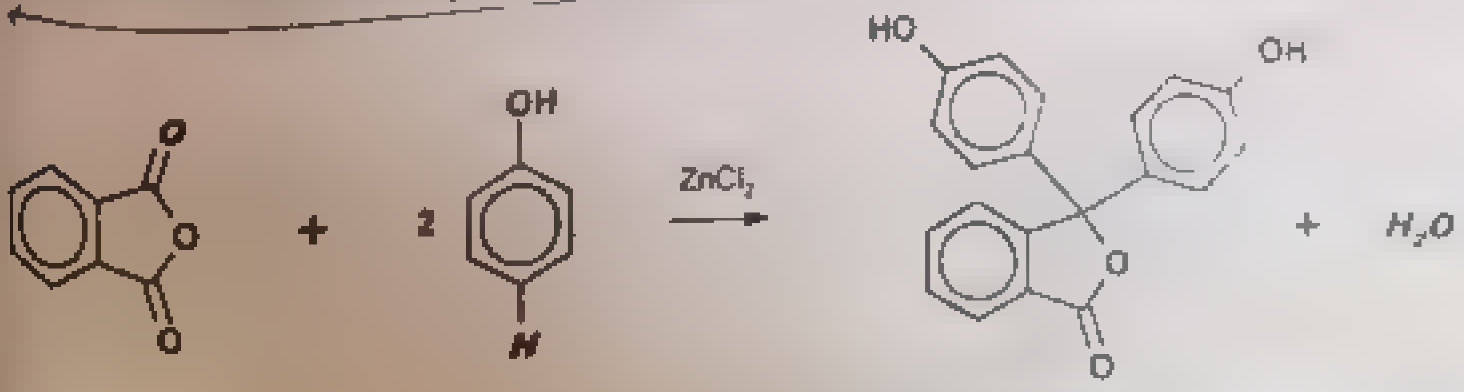
Phenolphthalein:

- It is also a triarylmethane dye but it ...
- It shows red colour in base and colourless in acid.



Phenolphthalein
(Colourless in acid)

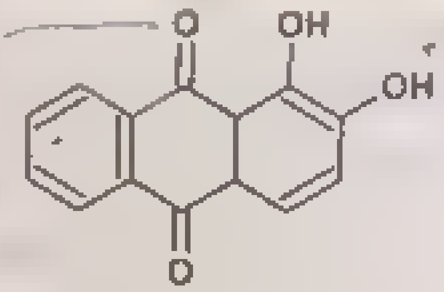
- Phenolphthalein is prepared by heating phthalic anhydride ... presence of anhydrous zinc chloride at 120°C



phenolphthalein

(4) ANTHRAQUINONE DYES:

- The para quinoid chromophore is present in these anthracene type dyes
- Alizarin is a typical anthraquinone dye.

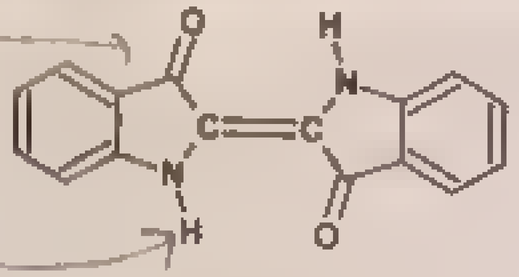


Alizarin

- Alizarin forms ruby red crystals which dissolve in alkali to give purple solutions
- It is used to dye wool and cotton

(5) INDIGO DYES:

- Indigo is an example of the type of dyes which contain carbonyl chromophore



Indigo

- It is a dark blue crystalline compound, insoluble in water
- It is used for dyeing cotton by the *Vat Process*

Exercise Q3 (iii) *What do you know about dyes? How are they classified on the basis of application?*

CLASSIFICATION OF DYES BY METHODS OF APPLICATION

- The chemical classification of dyes is of interest to the chemist but the dyer is concerned mainly with application of dyes to fabrics
- The method used for application in a particular case depends on the nature of both the dye and the fiber to be dyed
- The dyes are often classified on the basis of technique employed for their application

(1) DIRECT DYES:

- These can be applied to a fabric by direct immersion in a water solution of the dye
- A direct dye contains acidic or basic auxochrome which combines with the opposite polar group present in the chemical structure of the fiber.
- Wool and silk are readily dyed by this method
- Martius Yellow, a typical direct dye, has the acidic auxochrome -OH which interacts with the basic group of wool or silk

$$\underset{\text{(wool or silk)}}{\text{Fiber-NH}_2} + \text{HO-Dye} \rightarrow \text{Fiber-NH}_3^+ \ {}^-\text{O-Dye}$$

Exercise Q3 (iv) *Write a note on*
(a) Vat Dyes
(b) Mordant Dyes

(2) VAT DYES:

- These dyes are insoluble in water. However, on reduction with sodium hydrosulphide in a vat they give colorless soluble compound. This compound has a great affinity for cotton and other cellulose fibers

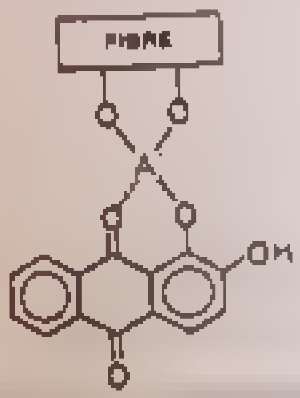
- The cloth is soaked in the solution of a ... with oxidants
- As a result, the colorless compound is oxidized back ... now bound to the fabric
- Indigo is a good example of a vat dye

- Indigo blue has auxochromes -OH which bind the dye fast to the cellulose fiber that contains ... by hydrogen bonding.

Exercise Q ... Write a note on
(c) Vat Dyes
(d) Mordant Dyes

(3) MORDANT DYES:

- This class of dyes has no natural affinity for the fabric and are applied to it with the help of salts e.g. oxides of aluminum or chromium. These salts are called Mordants
- A fiber such as cotton is first treated with a mordant and then with the dye
- The mordant forms an insoluble coordination complex between ... dye and binds the two
- The insoluble complex compound appears in the form of lakes that are ... light and washing
- The mordant dyeing is the most suitable for wool and nylon
- Alizarin is an example of a mordant dye.



* Auxochrome is ... functional group of atoms with non-bonding electrons when attached ...

$-N-N-$ → $-NH_2$ ...

(4) AZOIC DYES (INGRAIN DYES):

- In this method of dyeing, the water insoluble azo dye is produced ...
- The cloth is first soaked in the solution of a coupling reagent ...
- It is then immersed in the solution of an auxochromes
- The azoic dyeing is particularly suitable for cotton and ... also ... nylon

(5) DISPERSE DYES:

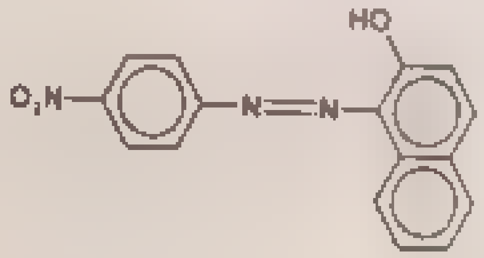
- These dyes are insoluble in water but can be dispersed in a colloidal form in ...
- The fabric is immersed in the colloidal dispersion of the dye
- The fine dye particles are absorbed into the crystal structure of the fabric
- Disperse dyes are used with modern synthetic fabrics such as nylon, orlon, polyester and cellulose acetate

* Chromophore ... of a molecule responsible ... its colour.

QUICK QUIZ-3

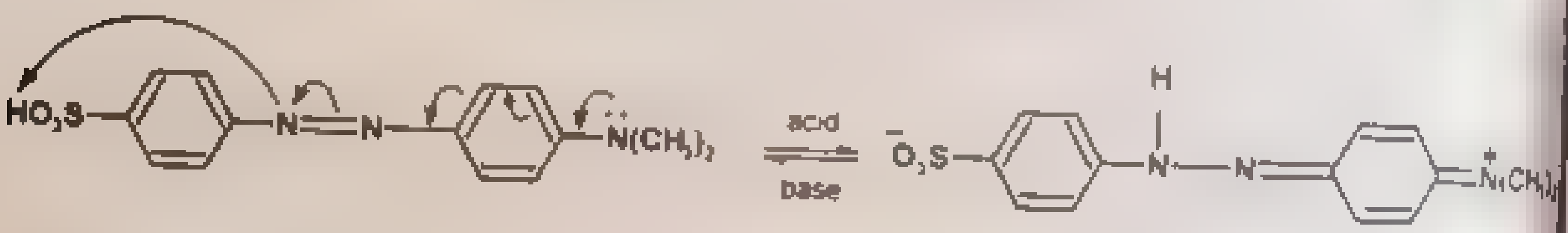
(1) Which one is first azo dye?

Para red is the first azo dye prepared by the reaction of diaz[illegible] itself



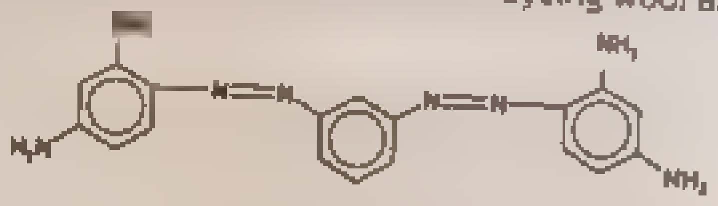
(2) What is the color of Methyl orange (i) in acidic medium (ii) in basic medium

- Methyl orange is used as indicator for acid base titrations. It is because [illegible] gives yellow color in base solution and red color in acid solution.
- The change in color is due to the change in the structure of the ions



(3) Which dye is used in boot polish and in dyeing wool and cotton?

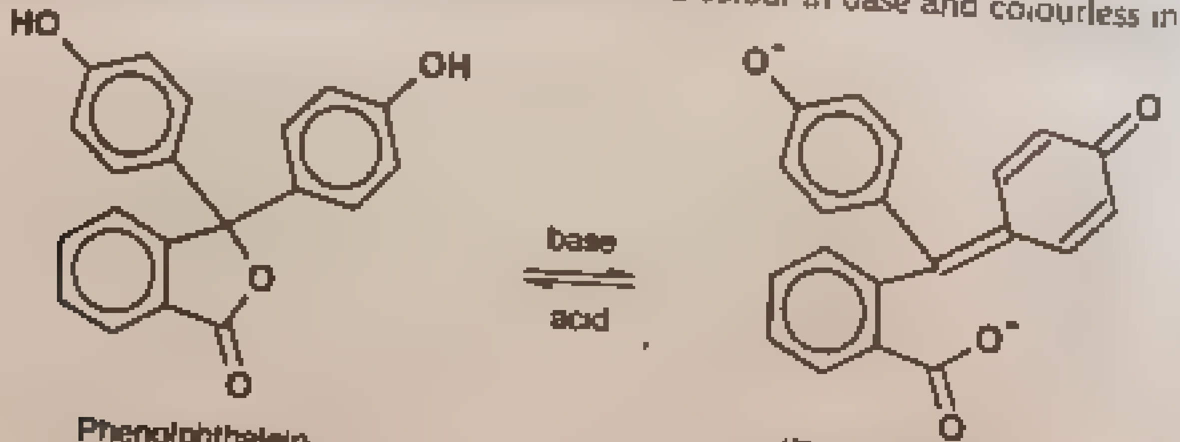
Bismarck brown is a brown dye used in boot polishes and for dyeing wool and cotton



Bismarck Brown

(4) What is the color of phenolphthalein in (i) acidic medium (ii) basic medium

- It is used as indicator in acid-base titrations. It shows red colour in base and colourless in acid



Phenolphthalein (Colourless in acid)

(Red in base)

Exercise Q3 (v) What is meant by Pesticides? Describe its types in detail

PESTICIDES

A pesticide is any chemical which is used by man to control pests. The pests may be [illegible] fungi, weeds, nematodes, snails, slugs, etc. Therefore, insecticides, fungicides, herbicides, etc., are all types of pesticides.

TYPES OF PESTICIDES

(1) INSECTICIDES

Insecticides are chemicals used to control insects.

- Often the word "insecticide" is confused with the word pesticide [illegible] types pesticides.
- An insecticide may kill the insect by touching it or it may have to be swallowed to be effective.
- Some insecticides kill both by touch and by swallowing.
- Insecticides called **Systemics** may be absorbed, injected or fed into the plant or animal to be protected. When the insect feeds on this plant or animal it ingests the systemic chemical and is killed.

(2) MITICIDES AND ACARICIDES

Miticides (or Acaricides) are chemicals used to control mites [illegible] and ticks.

- The chemicals usually must contact the mites or ticks to be effective.
- These animals are so many and small that great care must be used to completely cover the area on which the mites live.
- Miticides are very similar in action to insecticides and often the same pesticide kills both insects and mites.

(3) FUNGICIDES

Fungicides are chemicals used to control the fungi which cause molds, rots, and plant diseases.

- All fungicides work by coming in contact with the fungus, because fungi do not [illegible] sense.
- Therefore, most fungicides are applied over a large surface area to try to directly hit every fungus.
- Some fungicides may be systemic in that the plant to be protected may be fed or injected [illegible] chemical. The chemical then moves throughout the plant, killing the fungi.

(4) HERBICIDES

Herbicides are chemicals used to control unwanted plants.

- These chemicals are a bit different from other pesticides. It is because [illegible] growth of some plants, rather than to protect them.
- Some herbicides kill every plant they contact, while others kill only certain plants.
- It is of following types:

  Nonselective herbicides:

  ✓ These are toxic to all plants.

  ✓ These are often used when no plants are wanted in an area, e.g. nonselective [illegible] be used for clearing under guardrails or for total control [illegible]

  Selective herbicides:

  ✓ These kill some plants with little or no injury to other plants.

  ✓ Usually selective types will kill either broadleaved plants or grasses.

  ✓ These are useful for lawns, golf courses or in areas with desirable [illegible]

  ✓ Some very selective herbicides may kill only certain plants [illegible] e.g. [illegible] lawns.

(5) RODENTICIDES

Rodenticides are chemicals used to control rats, mice, bats and other rodents

- Chemicals which contr...
-
-
- They are usually appli...

(6) NEMATICIDES

Nematicides are chemicals used to control nematodes

-
-
-

(7) MOLLUSCICIDES

Molluscicides are chemicals used to control snails and slugs

-
- Baits are often used...

(8) REPELLENT

A repellent is a pesticide that makes a site or food unattractive to a target pest

- They a... in the...
- Insect repellents are available as ae... repel biting and...
- Vertebrate repellents are available as conce...
- They can be sprayed or painted on nursery crops... and seeds. Repelling deer, dogs, birds, raccoon...

QUICK QUIZ-4

(1) Differentiate between

(i) Pesticides and Insecticides

- *A pesticide is any chemical which is used by man to control pests.* The pests may be insects, plant diseases, fungi, weeds, nematodes, snails, slugs etc. Therefore insecticides, fungicides, herbicides etc. are all types of pesticides.
- *Insecticide is a type of pesticide. It is used to kill or control insects.*

(ii) Fungicides and herbicides

- Fungicides are chemicals used to control the fungi which cause molds, rots, and plant diseases.
- Herbicides are chemicals used to control unwanted plants.

(2) What do you understand by systemics

Systemics are chemicals which are made to enter into the body **system** of living organisms by different ways. These may be absorbed, injected or fed into the plant or animal to be protected. When the insect feeds on this plant or animal, it ingests the systemic chemical and is killed.

(3) How do herbicides different from other pesticides?

These chemicals are a bit different from other pesticides. It is because they are used to kill or slow the growth of some plants, rather than to protect them.

(4) Give different types of repellents

A repellent is a pesticide that ...

e.g. insect repellents are ...

repel biting and nuisance insects

(5) What are molluscicides

Molluscicides are chemicals used ...

Usually the chemicals must be eaten b...

in an area

PETROCHEMICAL

- The prefix "petro" ... "petroleum"
- since "petro-" is Ancient Greek for "rock" ... "oil". Therefore, the etymolog... "oleochemicals"
- However, the term ... derived from plant an...

Explanation

- Petrochemicals are ... petroleum
- Some chemical compou... obtained from other fossil f... or renewable sources such as ...

Exercise Q3 (vi) Describe the basic building block in petrochemicals technology

TYPES/CLASSES OF PETROCHEMICAL RAW MATERIALS (BUILDING BLOCKS):

Petrochemical classes are

(a) Olefins including ethylene and propylene

(b) Aromatics

(c) Synthesis Gas

- Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents and adhesives
- Primary petrochemicals are divided ... structure

(a) OLEFINS INCLUDING ETHYLENE AND PROPYLENE

- Olefins includes ethylene, propylene and ...
- At oil refineries olefins are produces ... chemical cracking such as steam cracking and by catalytic reforming
- Ethylene and propylene are important sources ... chemicals ... plastics products
- Butadiene is used in making synthetic rubber
- Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants and gels.

(b) AROMATICS

- Aromatics includes benzene, toluene and xylenes
- At oil refineries, aromatic hydrocarbons are mainly produced by catalytic reforming or similar processes
- Benzene is a raw material for dyes and synthetic detergents
- Benzene and toluene are raw materials for isocyanates
- Manufacturers use xylenes to produce plastics and synthetic fibers

(c) SYNTHESIS GAS

- Synthesis gas is a mixture
- Ammonia is used to make ... intermediate
- A very wide range of chem ... used in industry monomers ...
- Form the monomers ... gels are produced
- World is production of ethylene is arou ... of aromatic raw materials 70 m ... ton for ...
- The largest petrochemicals industrie ... growth in new production capacity ...
- There is a substantial inter-regional trade ...

LIST OF SIGNIFICANT PETROCHEMICALS AND THEIR DERIVATIVES

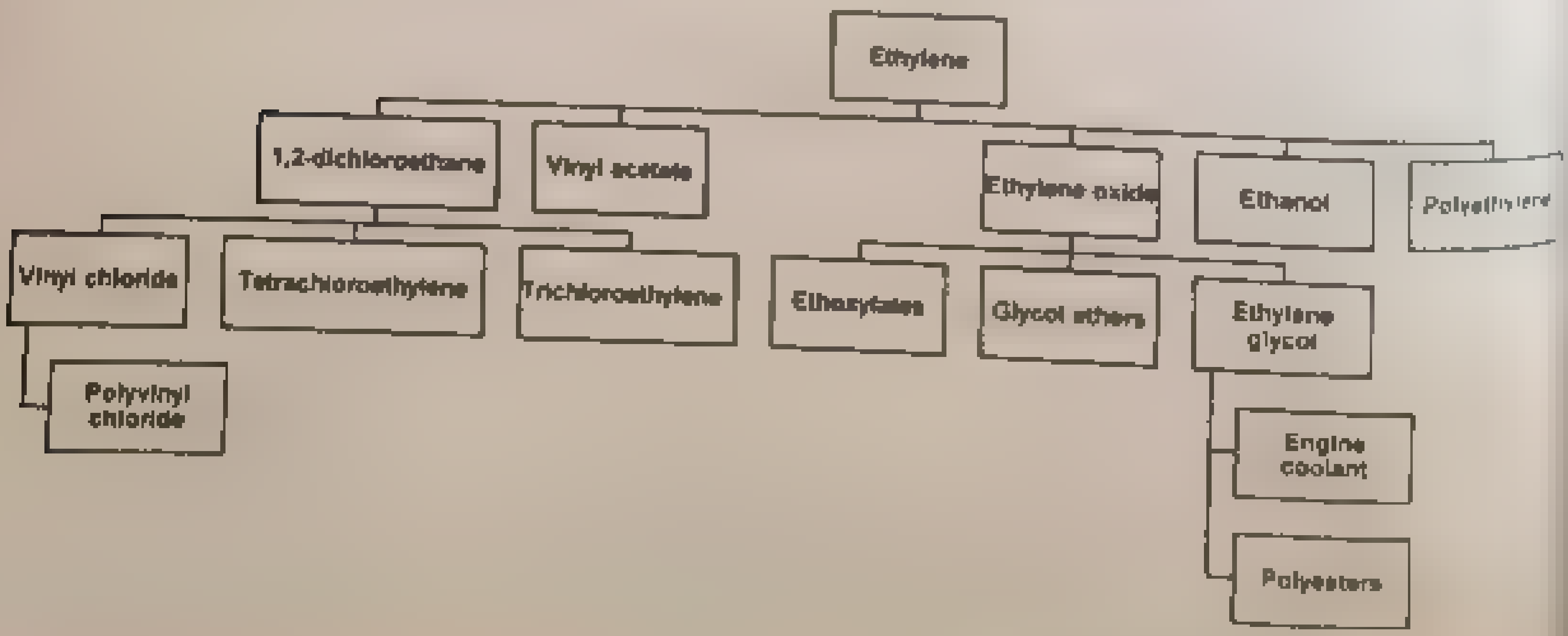
The following is a partial list of the major ...

Exercise Q2 (a) Enlist different chemicals produced from ethylene

CHEMICALS PRODUCED FROM ETHYLENE

Ethylene. The simplest olefin used as a chemical feedstock and ripening hormone
It is used to prepare following substances

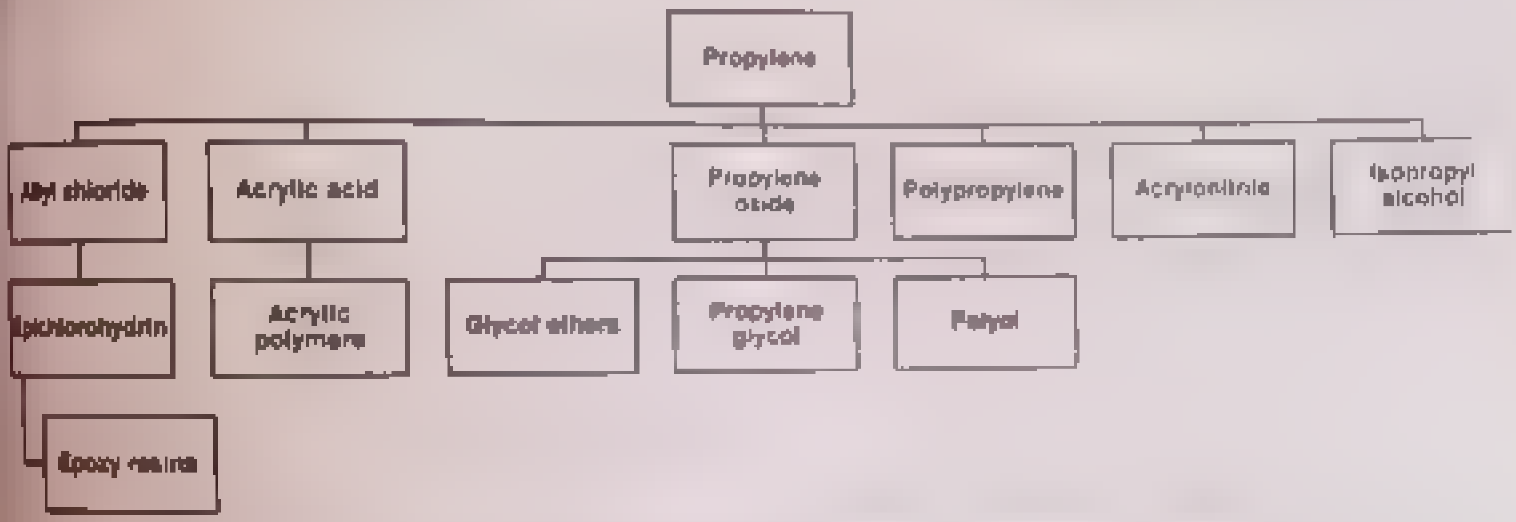
(i) ***Polyethylene:*** polymerized ethylene
(ii) ***Ethanol:*** via ethylene hydration (chemical reaction adding water) of ethylene
(iii) ***Ethylene oxide:*** via ethylene oxidation
 (a) *Ethylene glycol:* via ethylene oxide hydration
 Engine coolant: ethylene glycol, water and inhibitor mixture
 Polyesters: any of several polymers with ester linkages in the backbone chain
 (b) *Glycol ethers:* via glycol condensation
 (c) *Ethoxylates*
(iv) ***Vinyl acetate***
(v) ***1,2-dichloroethane***
 (a) *Trichloroethylene*
 (b) *Tetrachloroethylene:* also called perchloroethylene: used as a dry cleaning solvent and degreaser
 (c) *Vinyl chloride:* monomer for polyvinyl chloride
 Polyvinyl chloride (PVC) type of plastic used for piping, tubing, other things



CHEMICALS PRODUCED FROM PROPYLENE

Propylene It is used as a monomer and a chemical feedstock.
It is used to prepare following substances

(i) isopropyl alcohol - 2-propanol: often used as a solvent or rubbing alcohol
(ii) acrylonitrile - useful as a monomer in forming Orlon, ABS
(iii) polypropylene - polymerized propylene
(iv) propylene oxide
  (a) polyol - used in the production of polyurethanes
  (b) propylene glycol - used in engine coolant and aircraft deicer fluid
  (c) glycol ethers - from condensation of glycols
(v) acrylic acid: acrylic polymers
(vi) allyl chloride -
  (a) epichlorohydrin - chloro-oxirane; used in epoxy resin formation
    epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine [illegible]



CHEMICALS PRODUCED FROM BENZENE

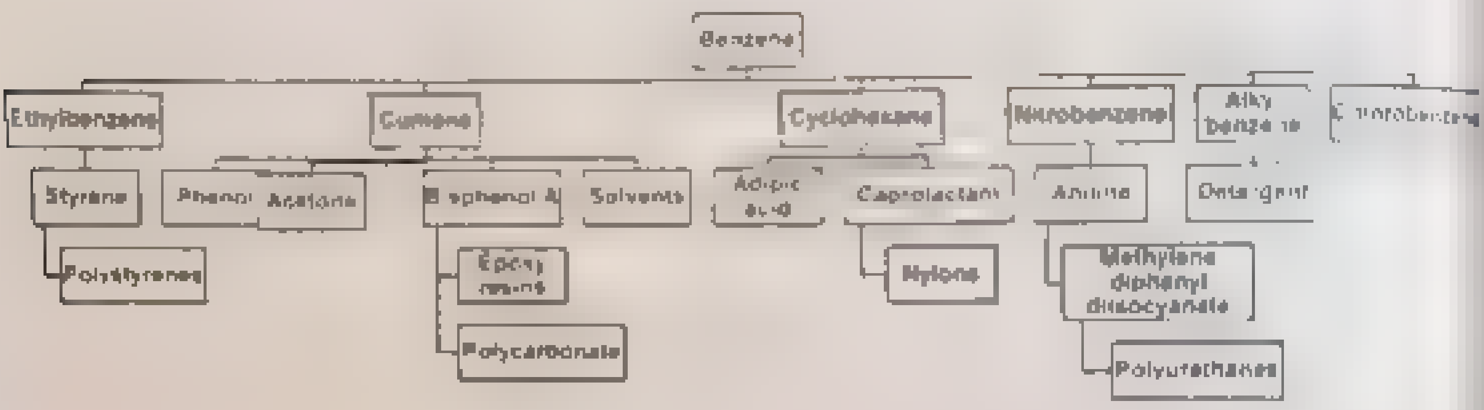
Benzene - the simplest aromatic hydrocarbon

(i) **ethylbenzene** - made from benzene and ethylene
  (a) styrene made by dehydrogenation of ethylbenzene, used as a monomer [illegible]
    polystyrenes - polymers with styrene as a monomer
(ii) **cumene** - isopropylbenzene, a feedstock in the cumene process
  (a) phenol - hydroxybenzene, often made by the cumene process
  (b) acetone - dimethyl ketone; also often made by the cumene process
  (c) bisphenol A - a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate
  - epoxy resins - a type of polymerizing glue from bisphenol A, [illegible] hardener
  - polycarbonate - a plastic polymer made from bisphenol A [illegible]
  (d) solvents - liquids used for dissolving materials; examples [illegible] ethanol, isopropyl alcohol, acetone, benzene, toluene [illegible]
(iii) **cyclohexane** - a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent
  (a) adipic acid - a 6-carbon dicarboxylic acid which can be a precursor used as a co[illegible] with a diamine to form an alternating copolymer form of nylon
  (b) caprolactam - a 6-carbon cyclic amide
  - nylons - types of polyamides, some are alternating copolymers formed [illegible] dicarboxylic acid or derivatives with diamines [illegible]

(iv) **nitrobenzene**

(e) **alkylbenzene**

(f) **chlorobenzene**

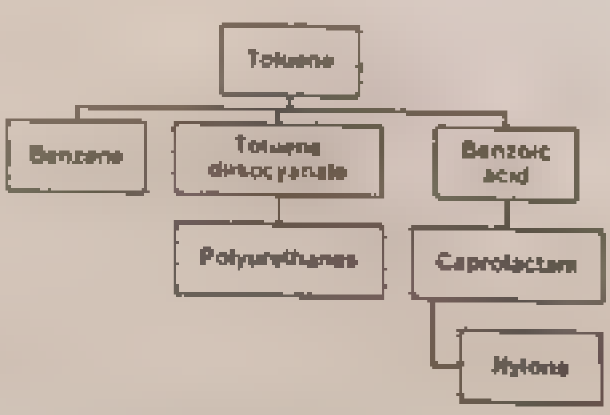


Exercise Q2 (vi) Enlist different chemicals produced from ethylene

CHEMICALS PRODUCED FROM TOLUENE

Toluene: methylbenzene, can be a solvent or precursor for other chemicals

- *(i)* ***benzene***
- *(ii)* ***Toluene diisocyanate (TDI)***, used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas
  - *(a)* polyurethanes - a polymer formed from diisocyanates and diols or polyols
- *(iii)* ***benzoic acid*** - carboxybenzene
  - *(a)* caprolactam
    - Nylons



Chemicals produced from xylenes

Mixed xylenes any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

- *(i)* ***ortho-xylene*** both methyl groups can be oxidized to form (ortho-)phthalic acid
  - *(a)* phthalic anhydride

(ii) meta-xylene

(a) isophthalic acid

- alkyd resins
- Polyamide Resins
- Unsaturated Polyesters

(iii) para-xylene - both methyl groups can

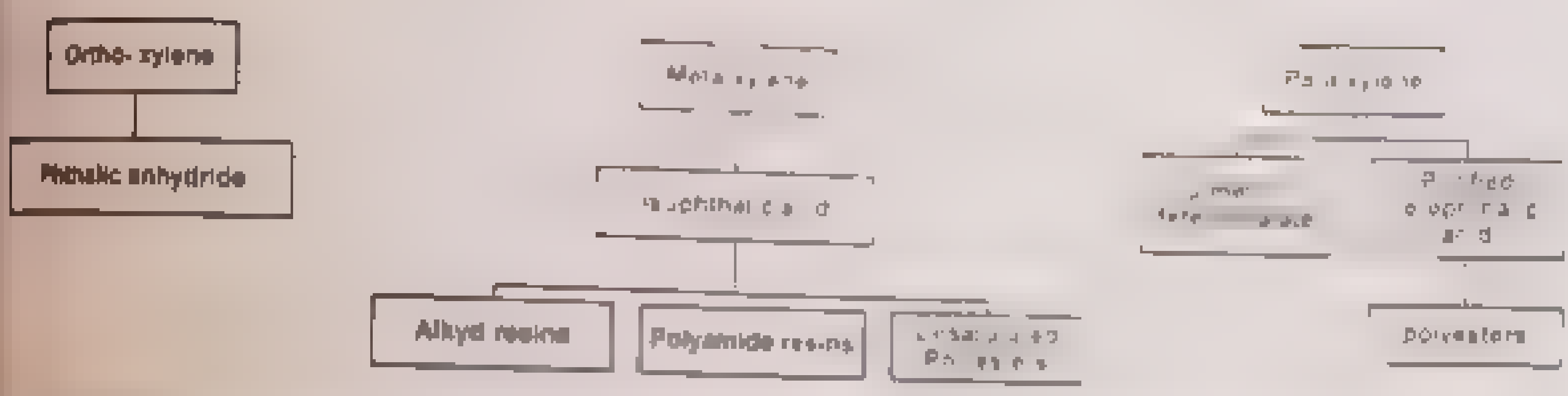
(a) dimethyl terephthalate can be

- *polyesters* although there

petrochemical products and

(b) purified terephthalic acid

- *polyesters*



QUICK QUIZ-5

(1) What do you mean by petrochemicals

Petrochemicals are chemical products derived from

Three important classes of petrochemicals are

(i) Olefins including ethylene and propylene **e.g**

(ii) Aromatics **e.g.** benzene, toluene and xylenes

(iii) Synthesis Gas **e.g.** a mixture of carbon monoxide

(2) What are classes of petrochemical raw materials

Three important classes of petrochemicals are

(i) Olefins including ethylene and propylene. **e.g**

(ii) Aromatics **e.g.** benzene, toluene and xylenes

(iii) Synthesis Gas **e.g.** a mixture of carbon monoxide and

(3) What are important fractions of petroleum

Important fractions of petroleum are

Petroleum gas, Gasoline ,Petrol) Naphtha Kerosene oil Diesel

(4) How does refining of petroleum carried out in Pakistan

- The oil obtained from the oil fields of Dhulian, Khaur, Balkassar is Fields Limited near Rawalpindi. The imported crude oil is
- The main refineries of Pakistan are
  - *(i)* Attock oil refinery
  - *(ii)* Pakistan oil refinery
  - *(iii)* National oil refinery
  - *(iv)* Pak-Arab refinery

SYNTHETIC POLYMERS

- Polymers are high mole[illegible] simple [illegible]
- The [illegible] monomers.
- The reaction by which [illegible]

Example

$$n\,H_2C{=}CH_2 \xrightarrow{\text{polymerization}} -CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$$

Ethylene (a monomer) — repeating unit — [illegible] (a polymer)

The formation of polyethylene from ethylene is an example [illegible]

- Polymers which are synthesized from only one kind of [illegible] are called **homopolymers**
- Polymers which are prepared from more than one kind of [illegible] called **copolymers**

CLASSIFICATION OF POLYMERS

There are two main types of polymers. Addition polymers and condensation polymers.

(I) ADDITION POLYMERS (CHAIN-GROWTH POLYMERS)

Addition polymers are formed by combination of alkenes monomers to produce a single huge molecule only.

- These reactions are catalyzed by peroxides or acids.
- The reactions require pressures of 1000 atmospheres at 200K
- Much lower temperatures and pressures can be used with so called **Ziegler Catalysts** [illegible] trialkyl aluminum and titanium tetrachloride in an inert solvent.

(a) POLYETHYLENE (POLYTHENE)

- Polyethylene has been produced commercially since 1943
- It is obtained by polymerizing ethylene.

In chain growth polymerization the monomers are added at one end of growing chain.

$$n\,H_2C{=}CH_2 \xrightarrow{\text{Polymerization}} \left[-CH_2-CH_2-\right]_n$$

Ethylene — Polyethylene

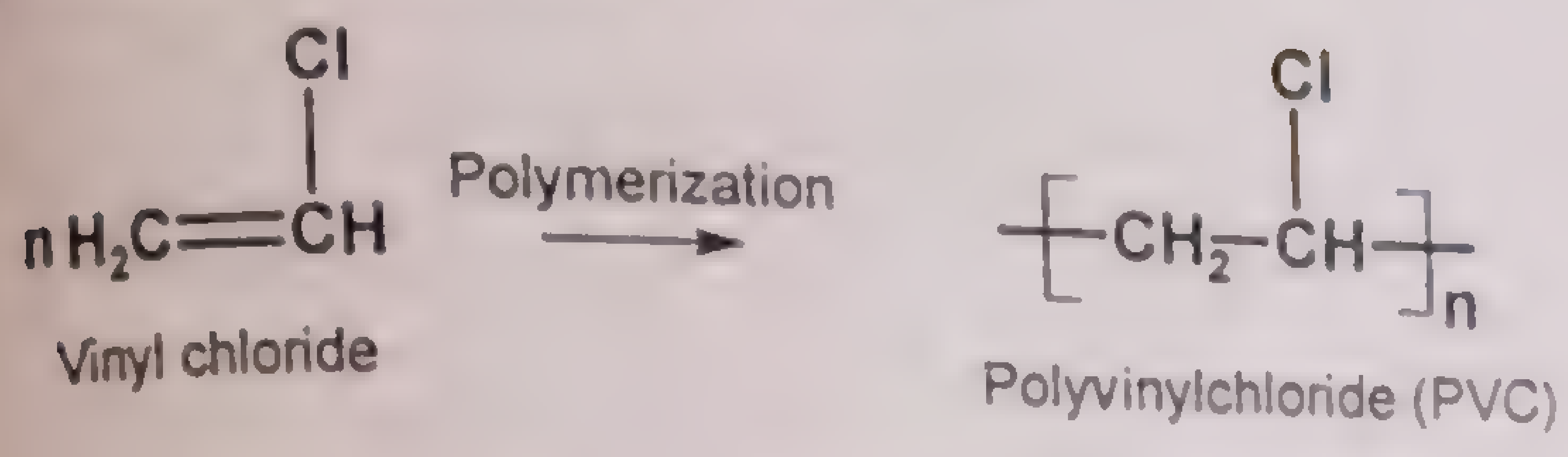
- Notice that the monomer (ethylene) contains a double bond and the polymer does not.
- The electrons of the monomer *pi* bond have moved and are used to link one monomer [illegible] by *sigma* bonds as indicated by extended lines in abbreviated polymer formula.
- The backbone of the polymer consists of the carbon atoms that originally formed the double bonds.
- Nothing is lost. The monomers simply add to each other.

Uses

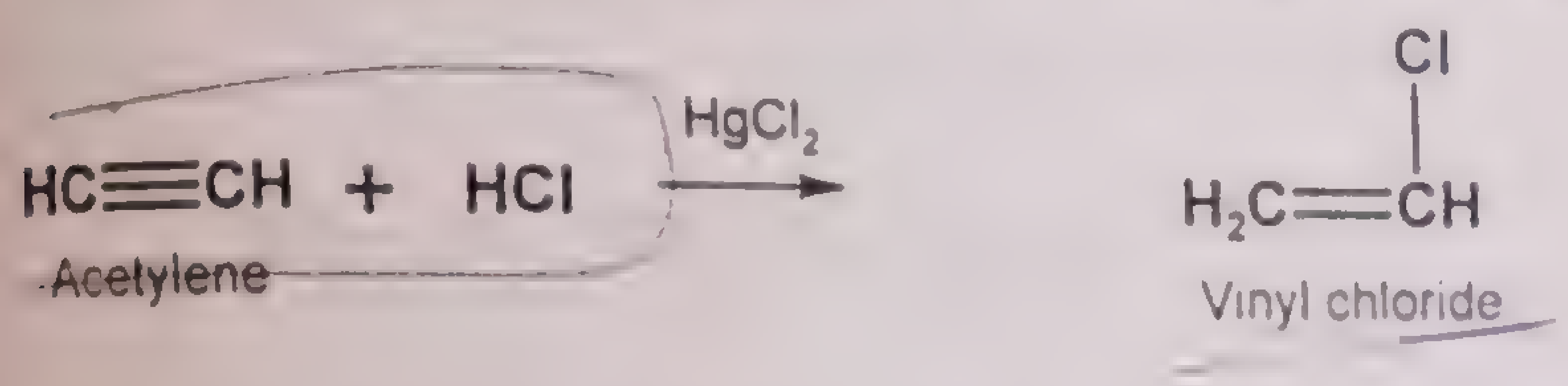
It is used in the manufacture of houseware such as buckets and dustbins, carpet backing, packing materials and cable insulation.

POLYVINYL CHLORIDE (PVC)

It is obtained by polymerizing vinyl chloride.



Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of $HgCl_2$



Uses

PVC is used in the manufacture of imitation leather, floor covering, corrugated roofing material and gramophone records.

(ii) CONDENSATION POLYMERS (STEP-GROWTH POLYMERS)

Condensation polymers are formed by combination of monomers with the elimination of simple molecules such as H_2O or CH_3OH.

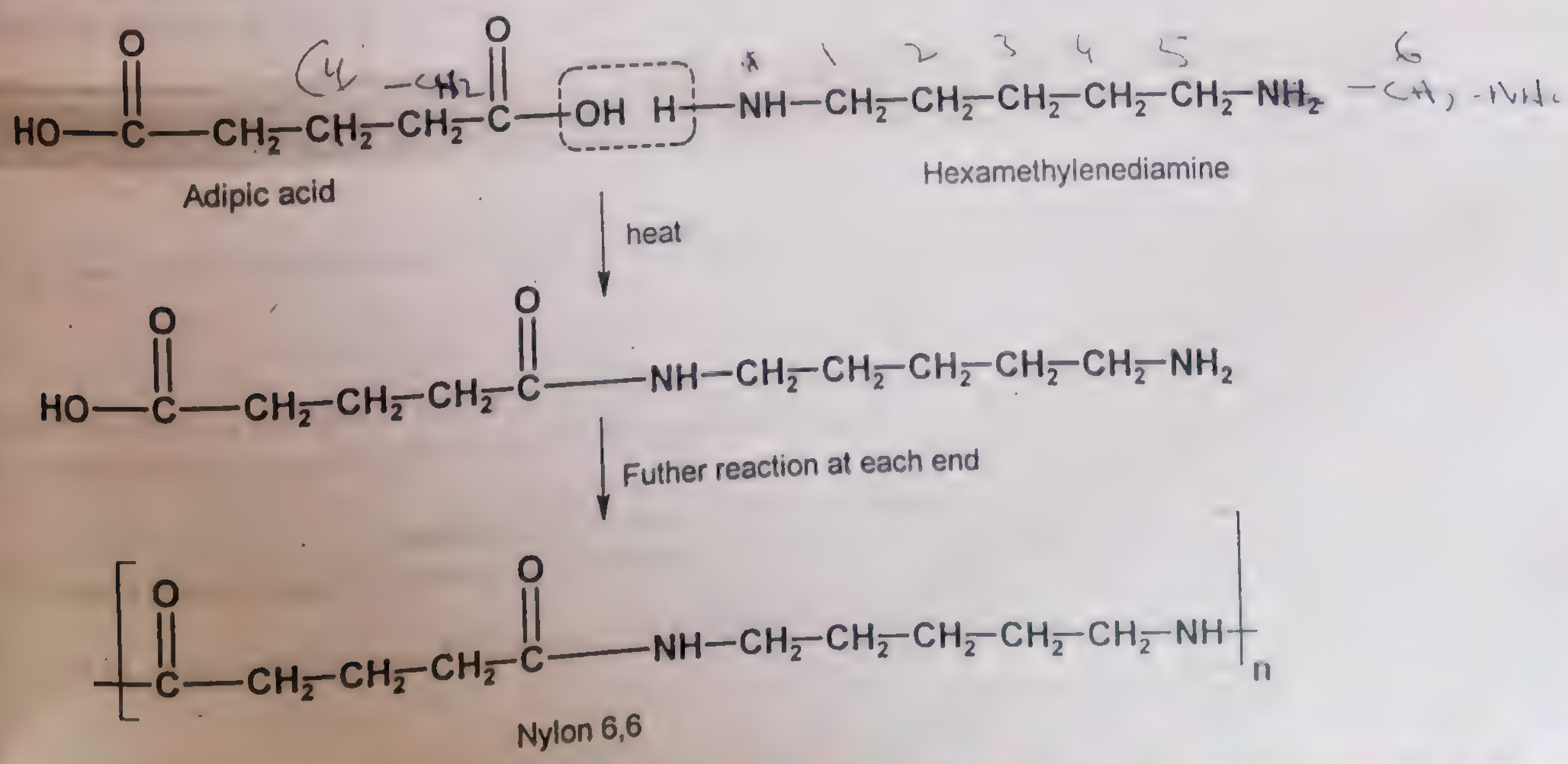
There are two main types of condensation polymers: Polyesters or Polyamides. The most common example is

> *In step-growth polymerization, first bifunctional compounds react together to form dimer, trimer, tetramer etc. and finally at the end all these unit together to form a polymer.*

Nylon-6,6

- It is the most important polyamide.
- It is obtained by heating adipic acid with hexamethylene diamine under nitrogen at 2000C.
- Nylon-6,6 derives its name from its starting materials, adipic acid and hexamethylene diamine, both of which have six carbons.

$NH_2 - (CH_2)_6 NH_2$



$NC-CH_2-CH_2-CH_2-CH_2-CN$

$NC-CH_2-CH_2-CH_2-CH_2-CN$

$\longrightarrow HOOC-CH_2-CH_2-CH_2-CH_2-COOH$

$\longrightarrow H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH_2$

THERMOPLASTIC AND THERMOSETTING POLYMERS

- [illegible]
- [illegible]

QUICK QUIZ-6

1. What are used [illegible]
   - PVC
     - [illegible] leather floor [illegible]
   - Nylon-6 6
     - [illegible] used as a synthetic fiber in the production of stocking and other wearing [illegible] fishing lines and ropes, bristles [illegible] gears and bearings.

2. **What is the difference between addition and condensation Polymers?**

   [illegible] of alkenes monomers to produce a single huge molecule [illegible]

   e.g. [illegible]

   [illegible] of monomers with the elimination of simple [illegible]

   e.g. [illegible]

Give difference between thermoplastic and thermosetting plastic

- A thermoplastic polymer is one which softens on heating and becomes hard on cooling e.g. Polyvinyl chloride PVC.
- A thermosetting polymer is one which becomes hard on heating it cannot be softened by heating, e.g Bakelite

How vinyl chlorid is prepared from acetylene

Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of HgCl

$$\underset{\text{Acetylene}}{HC\equiv CH} + HCl \xrightarrow{HgCl_2} \underset{\text{Vinyl chloride}}{H_2C=CH-Cl}$$

(i) Write forumula of

(i) adipic acid

$$HOOC-CH_2-CH_2-CH_2-CH_2-COOH$$

(ii) hexmethylene diamine

$$H_2N-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-NH$$

(i) Give use of Nylon-6,6

- Nylon-6,6 is developed as a synthetic fiber for the production of stocking and other wearing apparel
- It is used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes and molded objects such as gears and bearings

SOCIETY, TECHNOLOGY AND SCIENCE

DEVELOPMENT OF SYNTHETIC FIBERS

- Nylon is the first synthetic fiber
- Synthetic fibers are made from synthesized polymers or small molecules
- The compounds that are used to make these fibers come from raw materials such as petroleum based chemicals or petrochemicals. These materials are polymerized into a long linear chemical that bond two adjacent carbon atoms
- Different chemical compounds will be used to produce different types of fibers

Manufacturing of Synthetic Fibers. Melt-Spinning Process.

- There are several methods of manufacturing synthetic fibers but the most common is the **Melt-Spinning Process**
  - ✓ It involves heating the fiber until it begins to melt, then drawing out the molten fiber with tweezers as quickly as possible
  - ✓ The next step is to draw the molecules by aligning them in a parallel arrangement. This brings the fibers closer together and allows them to crystallize and orient
  - ✓ Lastly, is Heat-Setting. This utilizes heat to permeate the shape and dimensions of the fabrics ... from heat-sensitive fibers.
- In general, synthetic fibers are created by forcing, usually through extrusion (the act or process of shaping or thrusting out to create objects of a fixed, cross-sectional profile) fiber forming materials through holes (called spinnerets) into the air, forming a thread.
- Before synthetic fibers were developed, artificially manufactured fibers were ...

USES OF SYNTHETIC FIBRES

- Glass fibre [illegible]
- Metal [illegible]
- In the [illegible] industry [illegible] e.g.
  - phenolic resin foam

COSMETIC CHEMISTRY

Introduction

- The global market for skincare and color cosmetics exceeded 53 billion dollars in 2002
- The number of new products brought to market continues to expand exponentially
- Cosmetic chemists are always [illegible] and exotic ingredients that improve skin's appearance and health
- A vast [illegible] compounds is required to [illegible] these products
- The latest edition of the Cosmetics Toiletries and Fragrance Association (CTFA) Dictionary lists more than 10,000 raw materials
- Every year hundreds of new ingredients are added to the list of those that have been used for cosmetics

Following are the important cosmetics

(1) Nail Polish
(2) Nail Polish Remover
(3) Lipstick
(4) Hair dyes

NAIL POLISH

BACKGROUND

- Nail polish [illegible] lacquer or enamel is almost completely an invention of twentieth century technology. However other cosmetics have a history of hundreds or even thousands of years

- Nail coverings were not unknown in ancient ...
The upper classes of ancient Egypt ... composition, manufacture and handling ...
- Modern nail polish is sold in liquid form in small ...
- Within a few minutes after application, the ... fingernail. This coating is both water- and chip ...
- Generally a coating of nail polish may ...
- Nail polish can also be removed ... to break down and dissolve the polish.

Exercise Q3 (vii) *Describe raw materials and manufacturing process of Nail Polish*

RAW MATERIALS

There is no single formula for nail polish. The ...
These basic components include

(1) ***Film forming agents*** e.g. Nitrocellulose
(2) ***Resins and plasticizers*** e.g. castor oil ... acetic acids
(3) ***Solvents*** e.g. Butyl stearate and acetate co...
(4) ***Coloring agents*** e.g. "pearl" or "fish scale ...

THE MANUFACTRUING PROCESS

It includes following steps:

(1) When properly and fully milled, the mixture ... then broken up into small chips for mixing with the solvent. ... stainless steel ...

Caution:

This step is performed in a special room or area designed to con... ...in an area with walls that will close in if an alarm sounds and ... endangering the rest of the structure.

(2) At the end of the process, the mix is cooled ... perfumes and moisturizers.
(3) The mixture is then pumped into smaller, 55 gallon drums ... finished nail polish is pumped into explosion proof pumps ... retail market.

NAIL POLISH REMOVER

Nail polish remover base commonly contains a mixture of two ... ethyl acetate.
Acetone belongs to a group of organic molecules called ketones ... propanone. It is also sometimes called 2-propanone.
Ethyl acetate belongs to a group of organic molecules called esters ... ethyl acetate is ethyl ethanoate.

Interesting Information

Acetone is an organic liquid that is colorless, flammable and is ... miscible with water and nearly all other organic liquids.

QUICK QUIZ-7

(1) ***Give composition of nail polish***
The basic components include:
(i) ***Film forming agents*** e.g. Nitrocellulose

ii. **Resins and plasticizers**

iii. Solvents

iv. Coloring agents e.g.

(2) What is use of plasticizers in nail polish?

(3) In which material mixing of raw material of nail polish is prefe...

(4) What is nail polish remover?

acetate

(5) Give composition of nail polish remover

- Acetone ... acetone and ethyl acetate
- Ethyl acetate

LIPSTICK AND CHEMICAL COMPOSITION

- Lipsticks are simple ... composition however ...
- They are made up of ... ingredients—a waxy or fatty base, a dye ...
- There is no danger in the use of lipstick. In fact ...
- A...

RAW MATERIALS AND COMPOSITION

The primary ingredients found in lipstick...

(i) Wax (The wax used usually involves some combination of three types beeswax, candelilla wax or the more expensive carnauba wax,)
(ii) Oil (such as mineral, caster, lanolin, or vegetable oi
(iii) Alcohol
(iv) Fragrance and pigment,
(v) Preservatives and antioxidants

Generally the composition by weight is

- Wax and oil make up about 60 percent of the lipstick
- Alcohol and pigment make up 25 percent
- Fragrance added to lipstick, make up 1% or less of the mixture

THE MANUFACTURING PROCESS

The manufacturing process comprises of three separate steps

(i) melting and mixing the lipstick
(ii) pouring the mixture into the tube
(iii) packaging the product for sale

[illegible] and Mixing

- [illegible]
- [illegible]
  - [illegible]
  - [illegible]
  - [illegible]
- [illegible]
- [illegible] consistency is obtained.

[illegible]

- [illegible]
- [illegible]
- [illegible] removed
- The lipstick is cooled and [illegible]
- The lipstick then passes [illegible] the tube.

Labeling and Packaging

- After the lipstick is retracted [illegible]
- Labels identify the batch and [illegible]
- The final step in the manufacturing [illegible] packaging options available.

QUICK QUIZ-8

(i) Give composition of lipstick

Generally, the composition by weight is

- Wax and oil make up about 60 percent [illegible]
- Alcohol and pigment make up 25 percent [illegible]
- Fragrance added to lipstick, make up 1 [illegible]

(ii) What type of wax is used as raw material of lipstick

The wax used usually involves some combination [illegible] expensive carnauba wax.

(iii) How many steps are involved in manufacturing of lipstick

The manufacturing process comprises of three separate steps

(i) melting and mixing the lipstick

(ii) pouring the mixture into the tube

(iii) packaging the product for sale

(iv) Give percentage of alcohol and pigments in lipstick

Alcohol and pigment make up 25 percent by weight of the lipstick

HAIR DYE

HISTORY

1. Hair dye [illegible] of the oldest known beauty preparations, and was us[illegible] of the wo[illegible] peoples a[illegible] mention the use of hair c[illegible]
2. Early hair dyes wer[illegible]
3. Rock alum, quick[illegible] many parts of the world [illegible]
4. Many different [illegible] dyes
5. Indigo [illegible] shades of hair dye
6. An extract of the flowers of the chamomile plant was [illegible] many modern hair preparations.
7. The bark, leaves, or nutshells of many [illegible]
8. Other dyes were produced from walnut leaves or nut husks

MODERN AGE

- Preparations such as these were the only hair dyes available until the late nineteenth century.
- Hydrogen peroxide was discovered in 1818, but it was not until 1867 that it was exhibited at the Paris Exposition as an effective hair lightener.
- A London chemist and a Parisian hairdresser began marketing a 3% hydrogen peroxide formula at the Exposition as eau de fontaine de jouvence golden (golden fountain of youth water). This was the first modern chemical hair colorant.
- Advances in chemistry led to the production of more hair dyes in the late nineteenth century.
- The first synthetic organic hair dye developed was pyrogallol
- a substance that occurs naturally in walnut shells.

RAW MATERIALS

- In general, hair dyes include:
  - (i) **Dyes** e.g. 4-amino-2-hydroxytoluene
  - (ii) **Modifiers** e.g. resorcinol
  - (iii) **Antioxidants** e.g. sodium sulfite
  - (iv) **Alkalisers** e.g. ammonium hydroxide
- In addition to these basic chemicals, many different chemicals are used to impart special qualities. They may be shampoos, fragrances, chemicals that make the formula creamy, foamy, or thick, or contribute to the overall action of the formula.
- Hair dyes are usually packaged with a developer, which is in a separate bottle.
- The developer is most often based on hydrogen peroxide, with the addition of small amounts of other chemicals depending on the manufacturer.

THE MANUFACTURING PROCESS

The manufacturing process includes the following steps:

- First of all chemicals must be tested to make sure they are what they are labeled. Then weigh the chemicals accurately.

Further there chemicals are mixed in preheated water other solvents. The premix is agitated for about 20 minutes.

- The pre mix is then added to a large tank, containing the other in...
- After getting proper consistency this mixture is delivered ... pack with developer and then distributed in the market.

Exercise Q3 (viii) What are adhesives? Discuss its working and types

ADHESIVES

An adhesive is a compound that adheres or bonds two items together

- Adhesives are meant to stick things together.
- Adhesives may come from either natural or ... es are nature product and it is also manufactured in Factories.
- Some modern adhesives are extremely strong, and a ... modern construction and industry.

TYPES OF ADHESIVES:

(1) NATURAL ADHESIVES

- These are made from inorganic mineral sources ... able matter, starch (dextrin), natural resins, animal skin.
- They are often referred to as bioadhesives.

(2) SYNTHETIC ADHESIVES

Elastomers, thermoplastic and thermosetting ...

(3) DRYING ADHESIVES

The drying adhesives are a combination of ... adhesive hardens. e.g. White glue and rubber cement.

(4) CONTACT ADHESIVES

- Contact adhesives must be applied to both surfaces ... surfaces are pushed together.
- Some contact adhesives require as long as 24 hours ...

(5) HOT GLUE

- It is also known as "hot melt" adhesives.
- These adhesives are thermoplastics.
- They are applied hot and simply allowed to harden as they ...
- These adhesives have become popular for ... common materials to which they can adhere.
- The glue gun melts the solid adhesive and then ... onto the material where it solidifies.

(6) UV AND LIGHT CURING ADHESIVES

UV and light curing adhesives consist essentially of low ...

QUICK QUIZ-8

1. Define adhesives
[illegible]
(2) Give few examples of natural adhesives
[illegible]
3. Why and when drying adhesives harden
[illegible] e.g. [illegible]
4) How adhesives are used applied
- [illegible] e.g. [illegible]
- [illegible]
(5) How hot glue is applied?
Hot glue is applied hot and allowed to harden as the [illegible]
(6) Low molecular resins are present in which category of adhesive
UV and light curing adhesives consist essentially of [illegible]

KEY POINTS

- [illegible] of chemistry by discovering [illegible]
- Capital-intensive industries are [illegible] industries
- Light industries are easier to relocate than heavy industries and [illegible]
- Specialty chemicals are mainly used in the form [illegible] formulation. This calls for organic synthe[illegible]
- The polar auxochrome makes the d[illegible] the oppositely charged groups [illegible]
- Insecticides, fungicides, herbicides, etc., are all types of pesticides. Some pesticides [illegible] touch, the pest to be deadly. Others must be swallowed to be effective.
- Petrochemicals are chemical products derived from petroleum. Some chemical compounds [illegible] petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable s[illegible] as corn or sugar cane.
- ***Polymers which are synthesized from only one kind of monomer are called homopolymers.*** Polym[illegible] ***which are prepared from more than one kind of monomer are called copolymers.***
- A thermoplastic polymer is one which softens on heating and becomes hard on cooling.
- A thermosetting polymer is one which becomes hard on heating it can not be softened by heating.
- Modern nail polish is sold in liquid form in small bottles and is applied with a tiny brush.
- Nail polish remover base commonly contains a mixture of two organic solvents acetone and [illegible] acetate.
- Lipsticks are simple in chemical composition, however complicated their application or effects. The[illegible] made up of three ingredients—a waxy or fatty base, a dye and a perfume.
- Many different plant extracts were used for hair dye in Europe and Asia before the advent of mod[illegible] dyes.
- Elastomers, thermoplastic and thermosetting adhesives are examples of synthetic adhesives.

EXERCISE

Q1: Select the right answer from the choices given with each question.

(i) The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw material and their derivatives to products is called
(a) physical chemistry (b) classical chemistry (c) industrial chemistry (d) both b and c

(ii) Which dye is used in boot polish
(a) Azo dye (b) Congo red (c) Methyl orange (d) Bismarck Brown

(iii) Miticides are used to control
(a) ticks and mites (b) Fungi (c) Unwanted plants (d) mice and rats

(iv) Aerosoles and lotions are used as
(a) Fungicides (b) Repellent (c) Herbicides (d) a and c

(v) Petrochemicals are classified into how many classes?
(a) One (b) Two (c) Three (d) Four

(vi) How many classes of polymers?
(a) One (b) Two (c) Three (d) Four

(vii) Nylon is a polymer obtained by
(a) Addition polymerization (b) Condensation polymerization
(c) Homopolymer (d) None

(viii) Which of following is not a raw material for nail polish?
(a) Pearl (b) Castor oil (c) Resorcinol (d) Nitrocellulose

(ix) A polymer which becomes hard on heating is:
(a) Thermosetting (b) Thermoplastic (c) Addition (d) None

(x) Nail Polish remover base commonly contains a mixture of two organic solvents as
(a) Benzene and acetone (b) ethyl acetate and CS_2 (c) Benzene and CS_2 (d) acetone and ethyl acetate

(xi) Which of following adhesives are also known as bioadhesives?
(a) Drying adhesives (b) Synthetic adhesives (c) Natural adhesives (d) Hot glue

(xii) A chemical compounds which is meant to stick things together
(a) Nail polish (b) Lipstick (c) Hair dye (d) adhesives

(xiii) In early ages hair dyes were made from
(a) plants (b) animals (c) metallic compounds (d) both a and c

(xiv) Polymers which are prepared from more than one kind of monomer are
(a) homopolymer (b) copolymer (c) addition polymer (d) none

ANSWERS TO MULTPLE CHOICE QUESTIONS

(i) Ans: (c) industrial chemistry	**(ii) Ans: (d) Bismarck Brown**
By definition it is industrial chemistry	Bismarck Brown [illegible]
(iii) Ans: (a) ticks and mites	**(iv) Ans: (b) Repellent**
The chemicals which kills mites are called miticides	Aerosoles and lotions are [illegible]
(v) Ans: (c) Three	**(vi) Ans: (b) Two**
The three classes of petrochemicals are olefins, aromatics and synthesis gas	There are two main types of polymers Addition polymers and Condensation polymers
(vii) Ans: (b) Condensation polymerization	**(viii) Ans: (c) Resorcinol**
Nylon is polyamide. It is obtained by condensation of adipic acid and hexamethylene diamine with the loss of water	The raw materials for nail [illegible] Nitrocellulose
(ix) Ans: (a) Thermosetting	**(x) Ans: (d) acetone and ethyl acetate**
By definition it is thermosetting	Nail polish remover has [illegible] ethyl acetate
(xi) Ans: (c) Natural adhesives	**(xii) Ans: (d) adhesives**
Natural adhesives are obtained from living organisms i.e plants. So they are called natural adhesives	Adhesives bind or stick things [illegible]
(xiii) [illegible]	**(xiv) Ans: (b) copolymer**
Early hair dyes were made from plants, metallic compounds or a mixture of the two	Polymers made from two kinds of [illegible] copolymers

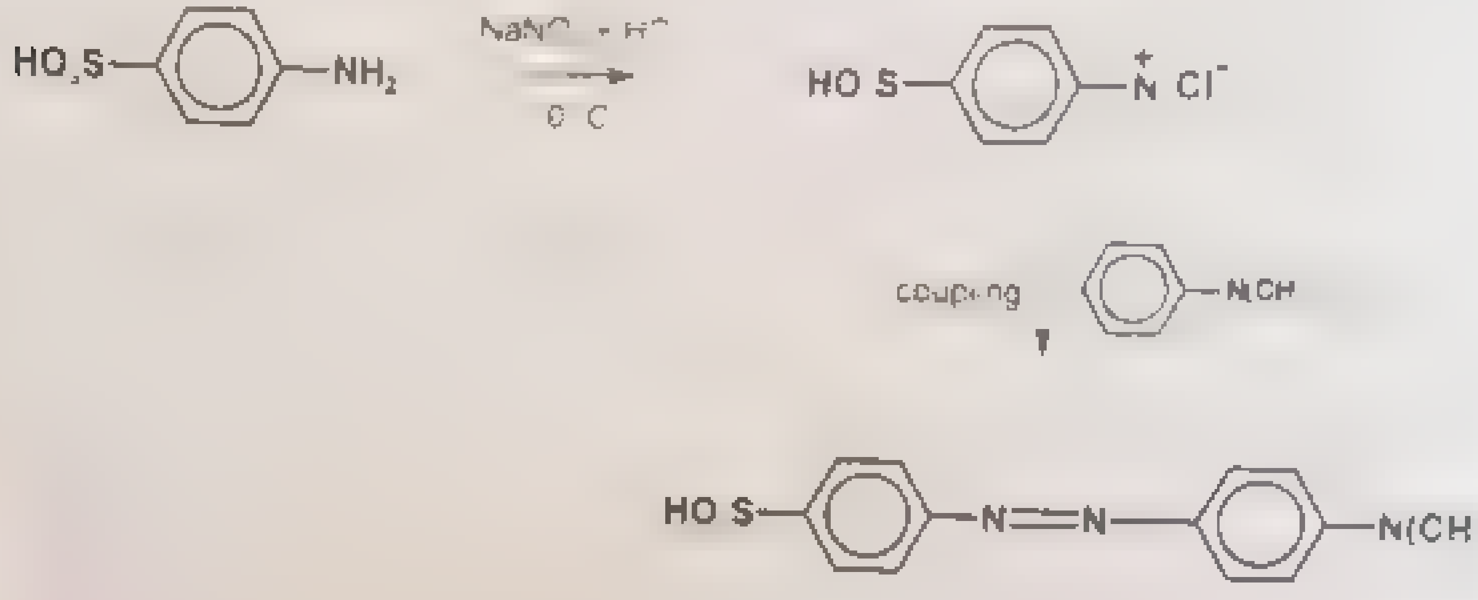
Q2: Give brief answers for the following questions.

(i) What is the difference between classical and industrial chemistry

- The Classical Chemistry (organic, inorganic and physical chemistry) [illegible] science of chemistry. It discovers and [illegible]
- The industrial chemistry applies physical and chemical [illegible] discovered by classical [illegible] towards the transformation of natural raw materials and [illegible] humanity.

(ii) How is methyl orange prepared?

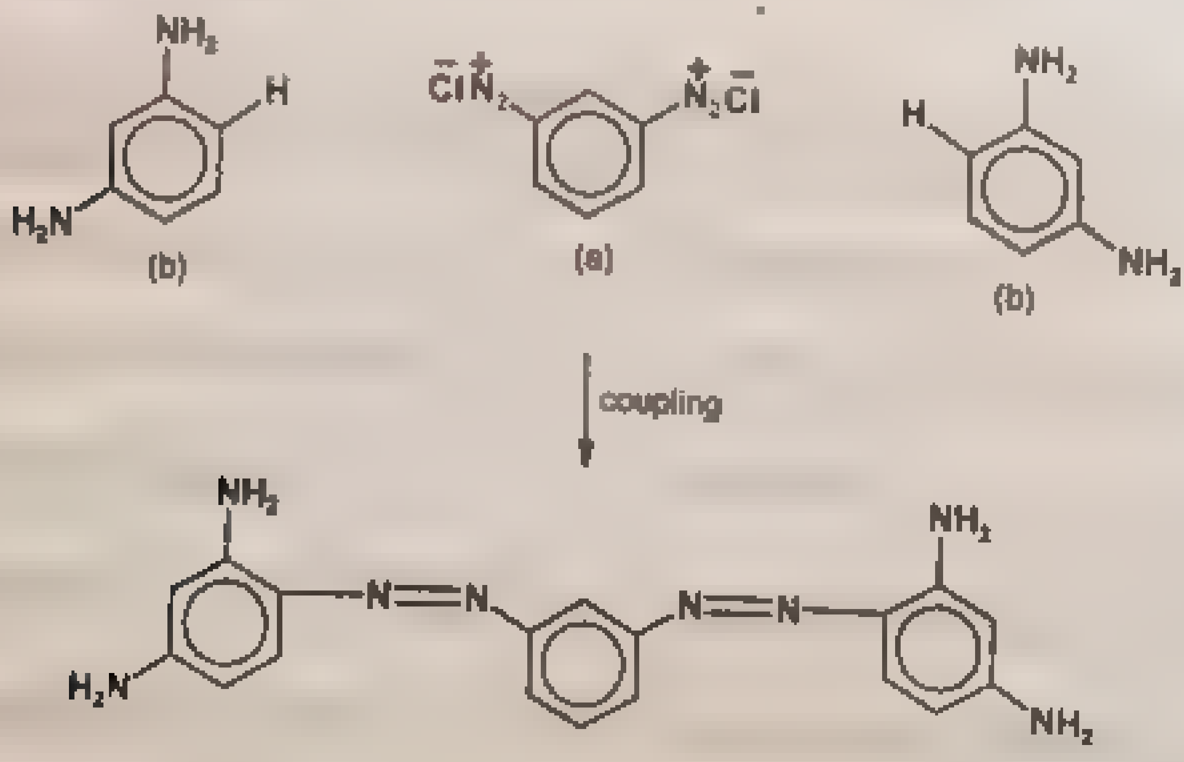
- Methyl orange is obtained [illegible]



methyl orange

(iii) How is Bismarck Brown prepared?

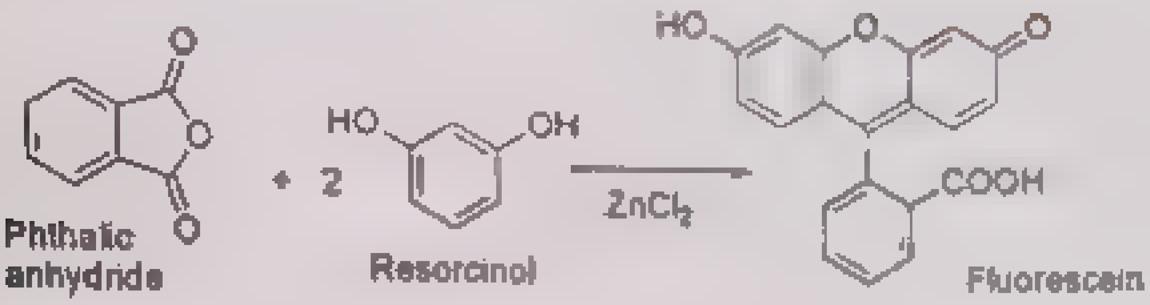
It is obtained by coupling tetrazotised m-diaminobenzene (a) with two molecules of m-diaminobenzene (b).



Bismarck Brown

(iv) How is Fluorescein prepared?

It can be prepared from phthalic anhydride and resorcinol ... the Friedel Crafts reaction.



(v) Enlist different chemicals produced from ethylene

Page

(vi) Write different chemicals produced from Toluene

Page

(vii) Differentiate between homopolymer and Copolymer

- Polymers which are synthesized from only one kind of monomer are called homopolymers e.g., Polyvinyl acetate

$$\underset{\text{Vinyl acetate}}{CH_2=\underset{|}{CH}-OCOCH_3} \longrightarrow -CH_2-\underset{OCOCH_3}{CH}-CH_2-\underset{OCOCH_3}{CH}-CH_2-\underset{OCOCH_3}{CH}-$$

Homopolymer (Polyvinyl acetate)

- Polymers which are prepared from more than one kind of monomer are called copolymers e.g.; vinyl acetate and butyl maleate combine to give a copolymer

$$\underset{\text{Vinyl acetate}}{\underset{OCOCH_3}{CH_2=CH}} + \underset{\text{Butyl maleate}}{\underset{COOBU}{CH}=\underset{COOBU}{CH}} \longrightarrow -CH_2-\underset{OCOCH_3}{CH}-\underset{COOBU}{CH}-\underset{COOBU}{CH}-CH_2-\underset{OCOCH_3}{CH}-$$

Copolymer

(viii) What is the difference between thermoplastic and thermosetting polymer

- A thermoplastic polymer is one which softens on heating and becomes hard on cooling e.g. Polyvinyl chloride (PVC)
- A thermosetting polymer is one which becomes hard on heating. It cannot be softened by heating e.g. Bakelite

(ix) How will you synthesize Nylon 6,6 from 1,3-Butadiene

Page 445

Q. Give detailed answers to the following questions.

(i) **What is chemical industry? Discuss different raw materials used in this industry**

Page 427

(ii) **What are dyes? How are they classified on the basis of structure?**

Page 430

(iii) **What do you know about dyes? How are they classified on the basis of application?**

Page 434

(iv) **Write a note on.**

(a) **Vat Dyes** *Page 434*

(b) **Mordant Dyes** Page 4..

(v) ***What is meant by Pesticides? Describe its types in detail***
Page 437

(vi) ***Describe the basic building block in petrochemicals technology***
Page 439

(vii) ***Describe raw materials and manufacturing process of Nail Polish***
Page 449

(viii) ***What are adhesives? Discuss its working and types***
Page 453

TEST YOUR SKILLS

Marks: 85

Time: 20 Minutes

Note: [illegible]

Marks: 17

a. Dyes

i) Raw materials are [illegible]

ii) An example [illegible]

(a) Methyl orange

[illegible]

(b) hydration

[illegible]

(a) one (b) two (c) three

xii) Which of the following is not a [illegible]

(a) Pear [illegible] (c) Resorcinol

xiii) In early days [illegible]

(a) paints [illegible]

xiv) A chemical compound which [illegible]

(a) [illegible] (b) [illegible] (c) [illegible] d. Adhesive

xv) [illegible]

(a) Dye [illegible] (c) [illegible]

xvi) In nail polish [illegible]

(a) water (b) butyl stearate

xvii) Which of the following solvent is used as [illegible]

(a) water (b) acetone [illegible]

Total Marks Sections B and C: 68

(ii) Time: 2:35 Hours

(a) Section B Marks [illegible] 42

Q2 Attempt any FOURTEEN parts. The answer to each part should not exceed 3 to 4 lines.

1 (a) What are commodity chemicals

(b) What are fine chemicals

(2) (a) Name main sources of raw materials [illegible]

(b) Which raw materials are obtained [illegible]

(3) (a) Differentiate between B [illegible] & B [illegible]

(b) Give examples of few natural [illegible]

(4) (a) What is meant by performance chem[illegible]

(b) Give share of different types of chem[illegible]

5 (a) What are requirements of process safety [illegible]

(b) Differentiate between classical & indus[illegible]

(6) What is a dye? Which properties it must have [illegible]

(7) Differentiate between

i) Pesticides & Insecticides

ii) Fungicides & herbicides

TOP Study

(8) (a) What are mollusc [illegible]

(b) Differentiate between selective & non – selective herbicides

(9) (a) What [illegible]

(b) Name [illegible]

(10) What [illegible]

(11) (a) Differentiate betw [illegible]

(b) Why Nylon 6 6 is ca [illegible]

(12) What are [illegible]

PVC [illegible]

(13) (a) How vinyl chlori [illegible]

(b) Write formula of a [illegible]

(14) (a) Define adhesive

(b) Give few examples of natural adhesives

(15) Give composition [illegible]

(16) (a) What is composition of [illegible]

(b) What type [illegible]

(17) (a) [illegible]

(b) [illegible]

(18) (a) [illegible]

(b) Give an example of a copolymer (01)

(19) (a) How will you prepare [illegible] from 1, 3 butadiene? (0[illegible])

(b) Give uses of Nylon 6 6 (02)

(01)

Section – C

Note Attempt any TWO questions. All questions carry equal marks. 2 × 13 = 26

1 (a) Wh [illegible]

(b) Wh [illegible]

(c) Write [illegible]

2 (a) How [illegible]

(b) Wh [illegible]

(c) [illegible]

3 (a) [illegible]

(b) [illegible]

(c) What are different [illegible]

04

CHAPTER # 23

ENVIRONMENTAL CHEMISTYRY

INTRODUCTION:

It is the branch of chemistry which deals with the chemicals and other pollutants in the environment resulting directly and indirectly from human activities.

It is the study of the sources, chemical reactions, transportation of the chemicals and their adverse effects on human beings.

Environment pollutant

Any substance in the environment, which adversely affects the human health, quality of life and the natural functioning of ecosystem, is known as environmental pollutant.

Primary Pollutants

The pollutants which directly comes into the atmosphere from the source are called primary pollutants

e.g. oxides of nitrogen and volatile organic compounds (VOCs) created from fossil fuel combustion etc.

Secondary Pollutants

The pollutants which are derived from primary pollutants by chemical reactions in the atmosphere are called secondary pollutants.

e.g. sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid, peroxyacetyl nitrate (PAN)

COMPONENTS OF THE ENVIRONMENT:

(1) Atmosphere: Gases surrounding the earth

(2) Hydrosphere. Concerned with all water bodies i.e. ocean, rivers, streams, lakes, glaciers and ground water reservoirs

(3) Lithosphere: Concerned with hard and rigid rocky [illegible]

(4) Biosphere: Area on earth with support life [illegible]

ATMOSPHERE:

- Our surrounding on earth is called atmosphere
- It consists of gases i.e. N_2, CO, He, Ne, Kr, Xe and water vapours
- Its thickness is about 1000 km above the surface of earth

The gases present in the atmosphere are very important in the following ways

(i) These gases absorb harmful radiations (cosmic rays and electromagnetic radiation) of Sun to protect life on earth. Otherwise these rays are very harmful to living things on earth

(ii) N_2 is used by nitrogen fixing bacteria

(iii) O_2 is necessary for breathing in animals

(iv) CO_2 is necessary for photosynthesis in plants and

(v) Water vapours are responsible for sustaining life on earth

- Atmosphere has been divided into four layers:

1 Troposphere 2 Stratosphere 3 Mesosphere 4 [illegible]

First two layer are of more concern to human life i.e. [illegible]

CHEMISTRY OF TROPOSPHERE:

- Troposphere is very close to earth in which we live
- It extends up to 20km it contains all those gases which [illegible]

SMOG

It is a combination [illegible] smoke and fog i.e. 'sm' from smoke and 'og' from fog

Industrial Smog

[illegible]

Photochemical smog

[illegible]

Major Chemical Pollutants in Photochemical Smog

Chemical	Sources (Natural and Human)	Environmental Effects	Additional Notes
Nitrogen Oxides (NO, NO_2)	[illegible]	[illegible]	[illegible]
Volatile Organic Compounds (VOCs)	[illegible]	[illegible] Causes [illegible] haze	[illegible]
Ozone (O_3)	[illegible]	[illegible] respiration, [illegible] eye irritation, decreased crop yield, retards plant growth, damages plastics, breaks down rubber [illegible]	[illegible] because [illegible] can only be daylight hours
Peroxyacetyl Nitrates (PAN)	[illegible] the reaction of NO_2 with VOCs [illegible] formed naturally in some [illegible]	[illegible] irritation, damaging [illegible]	[illegible]
Carbon Oxides (CO and CO_2)	[illegible] of [illegible] fuels (CO); [illegible] combustion of [illegible] of slush matter (CO); During the reaction in blast furnace; Cigarette smoke (CO); Burning of fossil fuels produce CO_2; [illegible]; Eruption of Volcanoes (CO); [illegible] of living organism	Causes [illegible] oxygen starvation results suffocation; Causes Green house and Global Warming results climatic changes; Causes Acid rain; Causes Acid rain; Respiratory irritation	
Oxides of Sulphur (SO_2, SO_3)	[illegible]	Causes acid rain; Respiratory irritation; Loss of green color in plants; Fading in color of Fabrics, leathers, paper and paints	

(b) CHEMISTRY OF PHOTOCHEMICAL SMOG (CHEMICAL REACTIONS IN THE ATMOSPHERE)

- The development of photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions.
- The following conditions must occur to begin the chemical process of photochemical smog development:
  - ✓ **Sunlight**
  - ✓ The production of **oxides of nitrogen (NOx)**
  - ✓ The production of **volatile organic compounds (VOCs)**
  - ✓ Temperatures greater than 18 degrees Celsius
- If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog.
- The formation of two most dominant toxic components, **ozone (O_3)** and **peroxyacetyl nitrate (PAN)** **is given below**. PAN is primarily created from volatile organic compounds.

- **Nitrogen dioxide** can be formed by one of the following reactions. The **nitrogen oxide** (NO) acts to remove ozone (O_3) from the atmosphere and this mechanism occurs naturally in an unpolluted atmosphere.

$$O_3 + NO \rightarrow NO_2 + O_2$$

$$NO + RO_2 \rightarrow NO_2 + \text{other products}$$

- Sunlight can break down **nitrogen dioxide** (NO_2) back into **nitrogen oxide** (NO)

$$NO_2 + \text{sunlight} \rightarrow NO + O$$

- The **atomic oxygen** (O) formed in the above reaction then reacts with one of the abundant oxygen molecules (which makes up 20.94 % of the atmosphere) producing **ozone** (O_3)

$$O + O_2 \rightarrow O_3$$

- **Nitrogen dioxide** (NO_2) can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as **peroxyacetyl nitrates** (PAN)

$$NO_2 + R \rightarrow \text{products such as PAN}$$

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by nitrogen oxide. The introduction of volatile organic compounds results in an alternative pathway for the nitrogen oxide. Although still nitrogen dioxide is formed but ozone is not consumed. Therefore ozone concentrations can be elevated to toxic levels.

QUICK QUIZ-1:

(i) What is environmental chemistry?

It is the branch of chemistry which deals with the chemicals and other pollutants in the environment, resulting directly and indirectly from human activities.

It is the study of the sources, chemical reactions, transportation of the chemicals and their adverse effects on human beings.

(ii) What is smog? What are its types?

It is a combination of smoke and fog i.e. "sm" from smoke and 'og' from fog"

It is of two types

Industrial Smog:

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog.

Photochemical smog

It is a condition th[illegible] primary pollutants (oxides of nitrogen and [illegible] created from fos[illegible] er the influence of sunlight to produce a mixture different and ha[illegible]

(iii) What are different sources and environmental effects of

a) Ozone

Sources [illegible] NO_2 [illegible] formed [illegible]

Environmental effects [illegible] respiratory irritation, eye irritation [illegible] retards plant growth, damages plastics, breaks down rubber, harsh odor

(b) Carbon oxides

Sources

The [illegible] bon oxides are:

- [illegible] plete combustion of carbon containing fuels (CO)
- [illegible] bustion of agricultural of slush matter (CO)
- [illegible] ction in blast furnace (CO)
- Cigarette smoke (CO)
- Bu[illegible] fuels [illegible] ce CO
- [illegible] ion of Soil CO_2
- [illegible]
- [illegible] CO

Environmental effects

[illegible] les have following environmental effects

- [illegible] xygen Starvation) result suffocation
- Causes Green house and Global Warming results climatic changes
- Causes A[illegible]
- Causes A[illegible]
- Respiratory irritation

(c) Sulphur oxides

Sources

The sources of sulphur oxides are

- Volcanic Eruption
- Burnt of oil & coal
- Sulphide ores are roasted

Environmental Effects

The sulphur oxides have following environmental effects

- Causes acid rain
- Respiratory irritation
- Loss of green color in plants
- Fading in color of Fabrics, leathers, paper and paints.

(iv) For the development of photochemical smog, what conditions are necessary?

The following conditions must occur to begin the chemical process of photochemical smog development

- **Sunlight**
- The production of **oxides of nitrogen (NOx)**
- The production of **volatile organic compounds (VOCs)**
- Temperatures greater than 18 degrees Celsius.

Exercise Q3 (i): Write a comprehensive note on acid rain

ACID RAIN

The pH of unpolluted rain water is 5.6. The rain water having pH less than ...

Explanation

We know that air contains SO_2, ...

(1) SO_2 present in air undergoes photolytic and catalytic oxidation to form SO_3 which reacts with ... or moisture to form H_2SO_4 i.e

$$SO_3 + H_2O \rightarrow H_2SO_4$$

(2) NO_2 reacts with rainy water or moisture ...

$$4N_2 + H_2O + O_2 \rightarrow 4HNO_3$$

$$2NO_2 + H_2O\ O_3 \rightarrow 2HNO_3 + O_2$$

(3) CO_2 reacts with rain water or moisture ...

$$CO_2 + H_2O \rightarrow H_2CO_3$$

(4) In some countries due to release ...

H_2SO_4, HNO_3 and H_2CO_3 ...

As far as H_2CO_3 is concerned ...

Quick Quiz-2 (ii): *Write down different effects of acid rain?*

IMPACTS OR EFFECTS

(1) It makes the lakes so a...
(2) The yield of agr...
(3) HNO_3 acid rain gradually eat...
(4) It fades the color of fabrics e.g ...
(5) Causes extensive leaf drop ...
(6) It is very corrosive and ...
(7) Acidification of soil and ... bodies. Then these ... eaten by fishes which prove ... dangerous for those animals and birds which ...
(8) It also damages steel, paint, ...

QUICK QUIZ-2

(i) What is acid rain?

The pH of unpolluted rain water is ...

(ii) Write down different effects of acid rain?

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(iii) List out those acid present in acid rain

The acids are: HCl, H_2SO_4, HNO_3 and H_2CO_3. However H_2CO_3 ...

(iv) Name those heavy metals which leach due to acidification of soil

Acidification of soil and rocks can ...

GREEN HOUSE EFFECT AND GLOBAL WARMING

The heating up of earth due to the trapping of infrared radiations (reflected from the earth's surface by CO_2 layer in the atmosphere is called "green-house-effect".

Explanation

- There is a protective layer O_3 gas in the atmosphere at ...

- Thus, the presence ... earth's surface ...
- In other words, we can say that the layer of CO_2 gas in the ... coming from the earth's surface. ... infrared rays coming from the ... raised. The rise in the ...
- The rise in the temperature produced by the green-house-effect in the ... the amount of CO_2 gas present in the atmosphere.

ORIGIN OF THE TERM "GREEN HOUSE EFFECT"

- This effect is used in horticulture for the ... roof are made of glass-sheet. This is called green house.
- The glass walls and glass roof of the house allow the short ... radiations, of sunlight, to go into green-house freely.
- However, these do not allow the long wavelength infrared radiations reflected by the soil, plants and other contents of the green-house to go out.
- These trapped infrared radiations raise the temperature inside the green house.
- Thus, even without the internal supply of heat, the temperature inside the green house becomes much ... than that outside it.

Quick Quiz-2 (ii) What is the importance of green house effect?

IMPORTANCE OF GREEN HOUSE EFFECT

- The green house effect is produced by the presence of CO_2 layer in the atmosphere. It is very necessary for our existence on the earth.
- Due to green house effect, CO_2 gas in the atmosphere does not allow the long wavelength infrared radiations reflected by the earth, to go out of the atmosphere. Hence the temperature of the earth surface and its atmosphere is increased.
- The rise in temperature of the earth is very necessary for our existence on earth. It is because without it the whole earth would be converted into extremely cold planet. Thus, we shall not be able to have a normal life.

Quick Quiz-2 (iii) Concentration of CO_2 is responsible for climate changes. Comment

EFFECT OF EXCESS OF CO_2 PRESENT IN THE ATMOSPHERE

- If the atmosphere contains too much quantity of CO_2, the green house effect is considerably increased.
- Thus, due to excess quantity of CO_2 present in the atmosphere, the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains), floods the low lying areas of the earth.
- It also changes the biological Activity of oceans and the patterns of cropping etc.

Thus the presence of the excess of CO_2 in the atmosphere brings about climate changes.

QUICK QUIZ-2

Is CO_2 responsible for green house effect? If yes then how?
Yes, CO_2 is responsible for green house effect. It is because ... radiations of longer wavelength. The layer of CO gas in the atmosphere traps ... coming from the earths surface. Thus energy of rays is trapped by CO_2. Hence ... is raised which is called Green House Effect.

What is the importance of green house effect?
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Concentration of CO_2 is responsible for climate changes. Comment
Page 497 Exercise Q 2 (ix)

AUTOMOBILE (POLLUTANTS AND CONVERTER)

- In automobiles during incomplete combustion of petrol ... pollute the atmosphere.
- The engine used in these motor vehicles are called internal combustion ... which is used as a fuel is burnt inside the engine and not separately.
- The exhaust gases contains CO, NO, NO_2, unburnt carbon ... compounds, some alcohol and acids.
- All theses substances are poisonous and hence pollute air.

PRODUCTION OF POLLUTANTS

- Petrol is used as a fuel in automobile car engine. The main ... hydrocarbons. These hydrocarbons have general formula C_nH_{2n} and hence are called ...
- Petrol burns very fast in a car engine. Due to short time available for ... combustion of petrol takes place and some CO, unburnt carbon particles, CO ... are produced.
- CO and carbon particles are emitted into the air and thus air is polluted.
- When petrol burns in a car engine, a very high temperature is produced.
- At this high temperature N_2 and O_2 present in air of the engine ... and form NO and NO_2. These gases also pollute the air.

Exercise Q3 (iii) How would you control air pollution? Describe different methods.

CONTROL MEASURE

In order to control the air pollution caused by hydrocarbons and CO etc. the following ...

i) By adding lead tetraethyl $Pb(C_2H_5)_4$ to petrol

- Suppose a vehicle uses petrol as fuel. Petrol burns very fast in the vehicle engine, e.g. ... combustion of petrol is very high and hence the time taken by the petrol for its combustion is ... Due to this short time, the combustion of petrol is incomplete.
- $Pb(C_2H_5)_4$ is added to the petrol to slow down the rate of combustion ...
- $Pb(C_2H_5)_4$ provides more time to the petrol for its combustion and hence enables it to burn ... completely.
- Due to this the quantity of unburnt hydrocarbons and CO coming out of ... is reduced and hence air pollution is also minimized.
- $Pb(C_2H_5)_4$ is oxidized to PbO which gets deposited on the spark plugs and ...
- In order to prevent the deposition of PbO, suitable amount of ... the petrol along with $Pb(C_2H_5)_4$.

- These halides convert PbO into $PbCl_2$ ... with the exhaust gases emitted by the vehicle ...

$$Pb(C_2H_5)_4 + O_2 + C_2H_4Cl_2 + C_2H_4Br_2 \rightarrow CO_2 + H_2O + PbCl_2 + PbBr_2$$

- Although the addition of $Pb(C_2H_5)_4$ minimize ... the air gets polluted with dangerous ...

(2) Catalytic oxidation/Converter

- The pollution of air caused by the exhaust ... a gas device with the vehicle ...
- In this device the exhaust gases ... burnt completely in the ... platinum catalyst before they are ...
- Hydrocarbons and CO are oxidized ...

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$
$$2CO + O_2 \rightarrow 2CO_2$$

The disadvantage of this method is that the ... gets poisoned by $PbCl_2$ ... are produced by the reaction between ... and $C_2H_4Br_2$ in the presence ...

QUICK QUIZ-3:

(i) What is the role of tetraethyl lead in minimizing the air pollution?

Petrol burns too fast in the engine. Thus, tetraethyl lead $Pb(C_2H_5)_4$ is added to the petrol to slow combustion. Thus, it gives more time to the petrol for its complete combustion. Hence the quantity of unburnt hydrocarbons and CO coming out of the engine, with exhaust gases is reduced. Hence air pollution is also minimized.

(ii) What is internal combustion engine

The engine used in these motor vehicles are called internal combustion engines. It is because the petrol which is used as a fuel is burnt inside the engine and not separately.

(iii) Name those pollutants produced in automobile engines

The exhaust gases from automobile engines contains CO, NO, NO_2, unburnt ... compounds, some alcohol and acids.

(iv) What gas is produced due to high temperature of engine

At this high temperature N_2 and O_2 present in air of the engine combine together and form NO and NO_2.

(v) What is drawback of lead tetraethyl used to control air pollution.

Tetraethyl lead $Pb(C_2H_5)_4$ is oxidized to PbO which gets deposited on the spark plugs and valves.

In order to prevent the deposition of PbO, suitable amount of $C_2H_4Cl_2$ and $C_2H_4Br_2$ are also added to petrol along with $Pb(C_2H_5)_4$.

CHEMISTRY OF THE STRATOSPHERE:

This layer of atmosphere is present 20-40 km above the earth and ozone is present in this layer at a height about 28 kilometers.

The concentration of ozone in this layer is 10 ppm (10 parts per million).

In this layer of atmosphere, ozone is most important.

PRODUCTION OF O_3 AND ITS TOXIC EFFECTS:

- O_3 is also produced in the upper part of the atmosphere by the action of sunlight on O_2.

$$3O_2 \rightarrow 2O_3$$

- Some O_3 is produced during various combustion processes taking place in the air.

- Traces of O_3 in air do not harm but O_3 of concentration more than 0.1 ppm is toxic and harmful to human beings
- O_3 also attacks rubber products

PROTECTIVE ACTION OF OZONE LAYER IN THE ATMOSPHERE:

- The thickest layer of O_3 exists at a height of 23 km from the surface of the earth
- The O_3 present in this layer absorbs harmful ultraviolet radiations coming from the sun
- If these radiations reach the earth, they will cause skin cancer and will destroy the organic molecules necessary for life
- Thus O_3 does not allow the ultra-violet radiations to reach the earth and thus saved from the harmful effects caused by these radiations
- If O_3 layer in the atmosphere disappears completely, then all the harmful ultra violet radiations coming from the sun would reach the earth. It would cause skin cancer in men and animals and will also damage the plants.
- Hence, All the life on earth would then gradually be destroyed

SOURCES OF DESTRUCTION/DESTROYING THE OZONE LAYER PRESENT IN STRATOSPHERE:

- In 1980 scientists showed that there is a hole in the O_3 layer
- This hole was detected over the region of Antarctica
- Due to the absence of O_3 layer, the ultraviolet rays coming from the sun can pass through the hole and thus can reach the earths' surface
- The ozone hole is due to the fact that the amount of O_3 present in stratosphere is getting reduced day by day. Thus, the ozone layer is becoming thinner and thinner
- The depletion of the ozone layer is due to the following sources

(1) Oxides of Nitrogen:

- The oxides of nitrogen present in the atmosphere decompose O_3 into O_2 and are themselves regenerated

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

- Thus, the presence of nitrogen oxides in the atmosphere destroys the ozone layer
- These oxides destroy about 70% of O_3 found in the stratosphere
- Greater is the amount of the oxides in the atmosphere greater is the percentage of O_3 which is destroyed

(2) Nuclear Tests:

Nuclear tests being conducted in the world generate high temperature
At high temperature, atmospheric nitrogen is favorably oxidized to NO
NO thus formed destroys ozone layer, as shown above

(3) Use of Chloro-Flouro Carbons:

Fluoro-chloro-carbons are the fluoro-chloro methanes like Freon 1 ($CFCl_3$) and Freon 2 (CF_2Cl_2)
These are stable compounds. These are chemically inert and hence do not react with the substances
These are used as aerosol spray propellants, refrigerants, fire-fighting reagent and solvents for cleaning electronic components
When they enter stratosphere, they absorb ultraviolet solar radiations and get broken down to release atomic chlorine. This atomic chlorine decomposes O_3 into O_2 like NO gas

$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

PROTECTION OF THE OZONE LAYER:

- [illegible]
- [illegible]
- [illegible]

SOME ALTERNATIVES TO CHLORO-FLUORO CARBONS (CFCs):

- [illegible] These have taken [illegible]
- HCFCs break [illegible] more easily [illegible] the atmosphere [illegible] stratosphere
- However because they [illegible]
- Much better substitutes for CFCs are [illegible]
- One of them CF_3CH_2F has been used [illegible] nearly all car air conditioners
- In electronic industries, soapy water followed by [illegible] clean micro circuits
- Unfortunately, a serious problem is associated with [illegible] contribute to climate change
- However researches are going on to find chemicals that are both effective [illegible] friendly

QUICK QUIZ-4:

i) Ozone acts both useful as well as harmful. Justify the statement.

The O_3 absorbs the harmful ultra-violet radiations coming from the sun. Thus, it saves the life from the harmful effects of ultra-violet rays.

However its high concentration in atmosphere is very harmful. It causes respiratory problems and rubber, retards plant growth etc.

(ii) Enlist the possible alternatives to the use of CFCs.

The possible alternatives to the use of chlorofluorocarbons (CFCs) are:

Hydrochlorofluorocarbons (HCFCs), e.g. CF_3CHCl_2 and CHF_2Cl

Hydrofluorcarbons (HFCs), e.g. CF_3CH_2F

(iii) How O_3 is decomposed by oxides of nitrogen.

The oxides of nitrogen present in the atmosphere decompose O_3 into O_2 and are themselves regenerated.

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

(iv) How ozone is produced.

O_3 is produced in the upper part of the atmosphere by the action of sunlight on O_2

$$3O_2 \rightarrow 2O_3$$

Some O_3 is produced during various combustion processes taking place in the air.

WATER POLLUTION AND WATER TREATMENT

The contamination of water with the substances which have adverse effects on human beings, animal and plants is called water pollution.

The substances whose presence in the water makes it polluted are called pollutants.

TYPES OF WATER POLLUTANTS

These are of following types

(I) SUSPENDED SOLIDS AND SEDIMENTS:

These are wastes which are not completely soluble but suspended in the water. These wastes include

(1) Oil spillage
(2) Live-stock waste
(3) Industrial wastes and
(4) Leather tanneries

Quick Quiz-5 (i) Briefly describe about oil spillage as a source of water pollution and its effects on environment.

(i) OIL SPILLAGE:

- Petroleum is a complex mixture of many compounds which are mainly hydrocarbons.
- It is transported from one place to another through sea.
- The petroleum products are used as
  (i) Fuel
  (ii) Lubricants manufacture of petrochemicals
  (iii) Plastics
  (iv) Electrical appliances
  (v) Synthetic rubber
  (vi) Detergents
- In order to prepare such a large varieties of substances, petroleum is handled on large scale in the world. So the oil spillage can take place and it creates serious problems.

Pollution of Water by Petroleum:

Water gets polluted by
  (i) accidental oil spills
  (ii) leakage from cargo oil tankers in sea
  (iii) tanker trucks
  (iv) pipelines leakage during offshore exploration
  (v) leakage of under ground storage tanks

Oil Spillage and Animal Life:

- Many petroleum products are poisonous and create serious health problems to
  (i) Humans
  (ii) Animals
  (iii) Aquatic life
- Polycyclic hydrocarbons are carcinogenic even at very low concentration.
- Marine animals are seriously affected by soluble aromatic fractions of oil.
- The spilled oil damages the feather of the birds or fur of animals and sometimes causes [illegible]

Petroleum and Under Water Plants:

- When oil is spilled on the surface of sea then the light transmission is affected. Thus, the process of photosynthesis of plants does not remain much efficient.
- Moreover, the concentration of oxygen in water is decreased.

2) LIVE-STOCK WASTE

3) INDUSTRIAL WASTES

Sources

Pollutants

- Oil greases. Mineral acids are also release in sma...

Effects of Industrial pollutants.

- When they are continuously ingested through food or wa... they get accumulated in the organisms ... cause serious health problems like anemia, kidney diseases, nervous disorder, high blood pressure etc.

(4) LEATHER TANNERIES

- There are many leather tanning units working in Pakistan. Their sizes vary from cottage scale to industrial units.
- Leather industries use chromium salts which have +6 oxidation state of chromium.
- Only a few industries have the facility of waste treatment. This can be done by reducing Cr oxidation states to Cr^{+3} oxidation state. Cr^{+3} is precipitated as $Cr(OH)_3$.
- Cr^{+6} salts are highly toxic and cause cancer.

DISSOLVED SOLIDS

These are wastes which are dissolved soluble in water completely. These wastes include

(1) Detergents
(2) Pesticides
(3) Chemical fertilizers

(1) DETERGENTS

- Detergents are used in homes and industries for washing
- After washing these detergents are thrown into water reservoirs. T
- he amount of detergents in reservoirs is increasing day by day
- This waste water containing detergents goes into rivers and finally reaches the ocean, which is harmful for life in seas.
- The detergents remove bound heavy metal ions like Pb, Cd and Hg and transport it from sediments to water. These metals particles are very toxic.

8) PESTICIDES

- The pesticides are both toxic and persistent.
- Analysis of polluted water has shown that it contains pesticides which are toxic to fish.
- **Endrin** is reported to be toxic for catfish and other varieties of fish even if present in traces.
- **D.D.T.** affects the central nervous system [illegible] toxaphene has been reported to cause bone degeneration in fish.

9) CHEMICAL FERTILIZERS

- Nitrate/phosphate salts are generally used as fertilizers to increase the yield of the crops.
- When these fertilizers are used in excess, some of their unused quantity is washed away from the agriculture lands into the ponds, lakes and [illegible] water. This water is polluted since it contains unused [illegible]
- Similarly the waste water coming [illegible] contains nitrogenous phosphatic fertilizers. When these are washed away [illegible] make the water polluted.
- The presence of nitrogenous phosphatic [illegible] the aquatic life and human beings in the following ways:
  - **(i)** The presence of the fertilizers in the [illegible] increases the growth of algae and other aquatic plants. These later on undergo decomposition [illegible] odor. These plants also deplete the amount of O_2 dissolved in water and [illegible] of aquatic life becomes difficult or impossible.
  - **(ii)** After a long period [illegible] are converted into swamps [illegible] and marshes. A marsh is an *area of land which is very wet and muddy.*
  - **(iii)** The water containing [illegible] polluted water cannot be purified for drinking purposes.

Exercise Q3 (iv): What is Thermal Pollution? Discuss its sources and environmental effects.

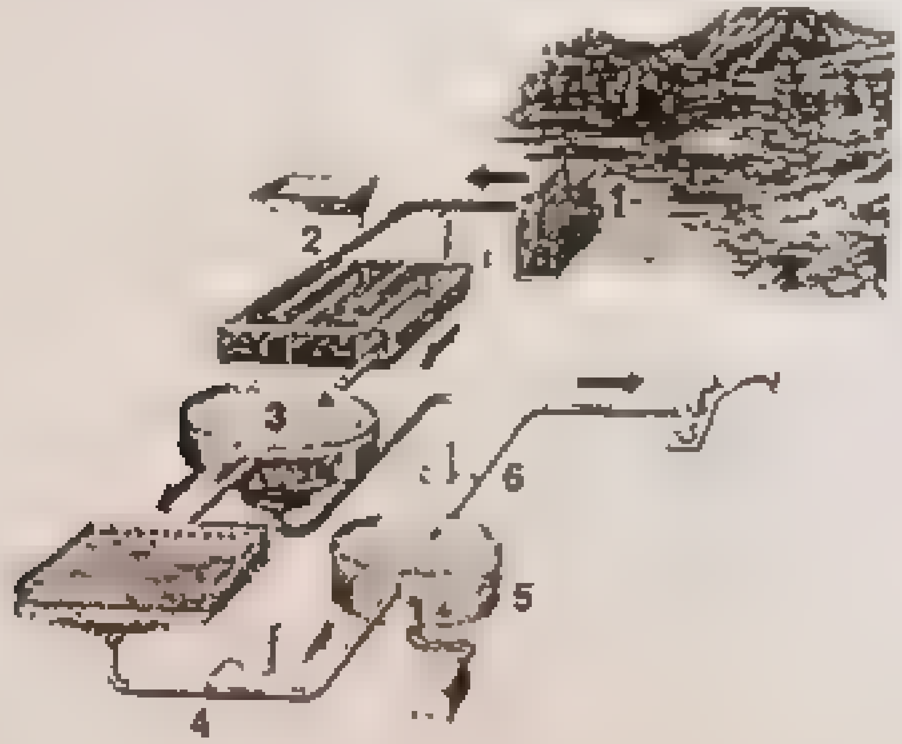
THERMAL POLLUTION

- Thermal pollution takes place because many electric generating [illegible] the process of cooling their generator. This heated water is then released [illegible] causing a warming trend of the surface water.
- Thermal pollution results when the heated effluent is released [illegible] In these cases permanent temperature increase often results which leads to decrease [illegible] of dissolved oxygen. In lakes it also becomes possible to bring about [illegible] summer stagnation periods.
- When heated water gets released into large well flushed [illegible] any permanent temperature rise.
- There are however problems related to the operation of plants using marine water for the cooling process.
- Evidence reveals that sea water tends to corrode the cooling pipes [illegible] generally constructed of a copper nickel alloy termed Monel. These metals read[illegible] dissolve in [illegible] heated seawater and are then released into the marine environment together with the heated effluent. This adds to the nickel and copper concentrations of these systems.
- In addition the screens covering the water intake pipes rapidly foul with marine organisms which decrease the flow of water into the plant. The screens have been commonly cleaned by using a concentrated detergent solution or copper sulfate. These cleaning materials have been then released into the contaminated the surrounding waters.

Exercise Q3 (c) What is waste water treatment? Discuss different methods of it

WASTE WATER TREATMENT: ANALYSIS/PURIFICATION OF WATER

- Industrial wastewater treatment covers the mechanisms and ... before its release into the environment or its re-use
- Most industries produce some wet waste. A... such production or recycle such waste within the production ...
- However many industries remain dependent on processes ...



Water Treatment Plant

Do You Know?
About 97% of the water on earth is found in the oceans. Most of the rest is frozen in the polar ice caps and in glaciers

TREATMENT OF INDUSTRIAL WASTE WATER

The different types of contamination of wastewater require a variety of strategies to remove the con...

(A) SOLIDS REMOVAL

Most solids can be removed using simple sedimentation techniques with the solids recovered as ... sludge

(B) OILS AND GREASES

- Many oils can be recovered from open water surfaces by skimming devices
- However hydraulic oils and the majority of oils that have degraded to any extent will a... or emulsified component. These require further treatment to eliminate

(C) SOFT ORGANICS

- Organic material of plant or animal origin is usually possible to treat using extended conventional ... water treatment processes
- Problems can arise if the wastewater is excessively diluted with washing water or is highly concentrated such as neat blood or milk
- The presence of cleaning agents, disinfectants, pesticides, or antibiotics can have detrimental impacts ... treatment processes

(D) HARD ORGANICS

- Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, coking products etc can be very difficult to treat.
- Treatment methods are often specific to the material [illegible]. Methods include distillation, adsorption, nitrification, incineration, chemical [illegible] or [illegible] disposal.

(E) ACIDS AND ALKALIS

- Acids and alkalis can usually be neutralized under controlled conditions.
- Neutralization frequently produces a precipitate that will require treatment as a solid residue that may also be toxic.
- In some cases, gasses may be evolved requiring treatment [illegible] the gas stream.

(F) TOXIC MATERIALS

- Toxic materials including many organic materials, metals (such as [illegible], silver, cadmium, thallium etc.) acids, alkalis, non-metallic elements (such as arsenic or [illegible]) are generally resistant to biological processes unless very dilute.
- Metals can often be precipitated out by changing the pH or by [illegible] other chemicals.
- Many, however, are resistant to treatment or [illegible] concentration followed by land filling or recycling.

QUICK QUIZ-5:

(i) *Briefly describe about oil spillage as a source of water pollution and its effects on environment.*
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(ii) *Enlist the diseases caused by live-stock*
Bacteria are present in the livestock waste. These cause different diseases like
(a) Dysentery, (b) Typhoid, (c) Hepatitis

(iii) *How industrial wastes pollute water?*
The industrial pollutants are highly toxic organic compounds and heavy metals like Pb, Cd, Cr, Hg, As, Sb etc. Oil greases, Mineral acids are also release in small quantities.
These pollutants result in contamination of water and make it unsuitable for irrigation and drinking purposes.

(iv) *How chemicals fertilizers polluted water?*
When Nitrate/phosphate fertilizers are used in excess, some of their quantity is washed away into the ponds, lakes and river with rain water and thus pollute the water.
The waste water coming from the fertilizer industries also contains nitrogenous and phosphatic fertilizers. When these are washed away into the lakes and river with rain water, they make the water polluted.

(v) *How solubility of oxygen in water is reduced by thermal pollution*
Thermal pollution occurs when the heated effluent is released [illegible] poorly flushed system. In these cases permanent temperature increase may occur which decreases the solubility of dissolved oxygen.

(vi) *What is swamp?*
A swamp is an area of very wet land with wild plants growing on it. It is generally a low lying area where water collects.

Various Parameters of Water Analysis

Following table will help us to determine the water qua[illegible]

Table [illegible]ater quality Indicators

Parameter	[illegible]	[illegible]
Dissolved oxygen	General indicator of water quality ; source of O_2 [illegible]	[illegible] rable fish
Total suspended solids	Clog fish g[illegible] reduce ligh[illegible]	[illegible]
Total dissolved solids	Repr[illegible] content which [illegible] may not be toxic	[illegible]
BOD	Amount of dissolved oxygen removed during decomposition of organic matter in a given time ; a general indicator of contamination due to biodegradable organics	[illegible] Water Status 1 [illegible] 2 [illegible] 3 mg liter Fairly clean 5 mg/liter Doubtful 10 mg/liter Contaminated
COD	Indicates the concentration of materials oxidizable by chemical reaction	0.5 mg liter indicates very clean streams
pH	Indicates the addition of acids or bases	pH depends on actual system
Iron	Excessive amounts can clog fish gills ; indicates drainage from iron-bearing sediments, mines, industrial processes	A maximum of 0.7 mg/liter for diverse fish populations
Manganese	Concentration low in natural systems due to low solubility , high concentrations indicates contamination	A maximum of 1 mg/liter is a common criterion for stream quality

Table (Contd.)

Parameter	*Significance*	*Level*
Copper	Indicates drainage from copper-bearing sediment, mines, plating, or other industrial sources	A maximum of 0.02-10 mg/liter is a common criterion for stream quality
Zinc	Indicates mine drainage or industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Hg, Cd, Pb, Ni, Cr, Ag, etc.	Indicates industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Nitrate	A major plant nutrient; in high-concentrations it can promote excessive plant growth; major sources are fertilizers, sludge, and sewage	A maximum of 0.3 mg/liter to prevent excessive fertilization of streams
Phosphate	A major plant nutrient; major sources are detergents, fertilizer, sewage	A maximum of 0.03-0.40 mg/liter total inorganic phosphate is a common criterion

QUICK QUIZ-6

(i) What is green chemistry

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is called green chemistry

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or the environment

(ii) Give importance of green chemistry

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or the environment. Thus it is effective in reducing the impact of chemicals on human health and the environment.

(iii) What is spinosad

Spinosad is an insecticide manufactured by fermenting a naturally occurring soil organism. It was registered by the EPA as a reduced-risk insecticide in 1997. It has following advantages

- It does not leach, bioaccumulate, volatilize or persist in the environment
- In fields, it left 70 to 90 percent of beneficial insects unharmed
- It has a relatively low toxicity to mammals and birds. It is slightly [illegible] toxic to aquatic organisms. However, it is toxic to bees.

(iv) Give principle of green chemistry.

The de[illegible]

[illegible]

(v) What is [illegible]

[illegible]

(vi) Give use [illegible]

[illegible]

Exercise Q1 [illegible]

GREEN CHEMISTRY

The te[illegible]

The design of [illegible] products and processes that reduce or eliminate the use and generation of ha[illegible] substances is called green chemistry.

- [illegible]
- [illegible]

WHY GREEN CHEMISTRY?

- Green chemistry is effective in reducing the impact of chemicals on human health and the envir[illegible]
- [illegible] companies have [illegible] cheaper and [illegible] profitable [illegible] higher efficiency [illegible] better product quality, and reduced [illegible]
- Many [illegible] laws and regulations [illegible] chemicals and following [illegible] can be complicated.
- But green chemistry allows companies to comply with the law in much simpler and cheaper ways.
- Finally, green chemistry is a fundamental science based approach. Addressing the problem of hazard[illegible] molecular level it can be applied to all kinds of environmental issues.
- Since 1991, there have been many advances in green chemistry, in both academic research and indus[illegible] implementation.
- For example, **Spinosad**, an insecticide manufactured by fermenting a naturally occurring soil organism [illegible] registered by the EPA as a reduced risk insecticide in 1997.
- Spinosad does not leach, bioaccumulate, volatilize, or persist in the environment and in field tests left [illegible] 90 percent of [illegible] insects unharmed. It has a relatively low toxicity to mammals and birds and is sl[illegible] to moderately toxic to aquatic organisms, but is toxic to bees until it dries.

(iv) Give principle of green chemistry

The design of [illegible]

[illegible] environment

(v) What is synthetic efficiency

An eff[illegible]

prod[illegible]

(vi) Give use of renewable feed stocks

Renewable fee[illegible]

[illegible]

Exercise Q3 [illegible] Green Chemistry

GREEN CHEMISTRY

The ter[illegible] 1991 is defined as

The design of chemical products and processes that reduce or eliminate the use and generat[illegible] substances is called green chemistry

- Green chemistry emphasizes [illegible]esign and creation of chemicals that are not hazardous to peo[illegible] environment
- It has been appl[illegible] industrial and consumer goods including pa[illegible] pesticides, plastics [illegible] cleaning energy generation and water p[illegible]

WHY GREEN CHEMISTRY?

- Green che[illegible] reducing the impact of chemicals on human health and the e[illegible]
- In addition many companies have found that it can be cheaper and even profitable to mee[illegible] goals Pro[illegible] higher efficiency less waste better product quality and reduced [illegible]
- Many [illegible] laws and regulations target hazardous chemicals and following all th[illegible] can be [illegible]
- But green chemistry allows companies to comply with the law in much simpler and cheaper wa[illegible]
- Finally green chemistry is a fundamental science based approach Addressing the problem [illegible] molecular level it can be applied to all kinds of environmental issues
- Since 1991 there have been many advances in green chemistry in both academic research a[illegible] implementation
- For example **Spinosad** an insecticide manufactured by fermenting a naturally occurring soil o[illegible] registered by the EPA as a reduced-risk insecticide in 1997
- [illegible] to bio accumulate volatilize or persist in the environment and in field [illegible] [illegible] insects [illegible] harmed It has a relatively low toxicity to mammals and birds and [illegible] to moderate[illegible] aquatic organisms but is toxic to bees until it dries

THE TWELVE (12) PRINCIPLES OF GREEN CHEMISTRY

- The aim of green chemistry is to reduce chemical related impact on human health and virtually eliminate contamination of the environment through dedicated sustainable prevention programs.
- Green chemistry searches for alternative environmentally friendly reaction media and at the same time strives to increase reaction rates and lower reaction temperatures.
- Sigma-Aldrich is dedicated to providing alternative products designed with the health and safety of its employees, customers, and the public in mind.
- The green chemistry concept applies innovative scientific solutions to solve environmental issues posed in the laboratory.
- **Paul T. Anastas** an organic chemist working in the Office of Pollution Prevention and Toxins at the EPA and **John C. Warner** developed the Twelve Principles of Green Chemistry in 1991.
- The twelve Principles focus on reducing the volumes of chemicals used and pollution prevention.
- These principles can be grouped into 'Reducing Risk' and 'M[illegible]g the Environmental Footprint'.

(i) REDUCING RISK IN THE LABORATORY

This group includes four principles

(1) ***Use Safer Chemicals*** – Utilize performance chemicals that have the lowest levels of toxicity.

(2) ***Design Less Hazardous Synthesis Methods*** – Where feasible, make use of synthetic or biosynthetic methods that pose little or no toxicity to human health and the environment.

(3) ***Use Safer Solvents and Reaction Conditions*** – Search for the most up-to-date information on green solvents that will optimize your process and provide a safer working environment.

(4) ***Accident Prevention*** – Select substances that minimize the pote[illegible] explosions, [illegible]res and chemical releases into the environment.

(ii) MINIMIZING THE ENVIRONMENTAL FOOTPRINT

This group includes eight principles

(1) ***Waste Minimization and Prevention*** – Develop chemical synthesis techniques [illegible] waste. It is better to prevent waste than to clean it up after its creation.

(2) ***Use of Catalysts Instead of Stoichiometric Quantities*** – Catalytic reactions [illegible] quantities of chemicals to carry out a specified transformation.

(3) ***Reduce the Use of Chemical Derivatives*** – The use of protecting groups or other forms of temporary modification of a functionality adds to the total waste incurred in a synthetic route.

(4) ***Synthetic Efficiency (Atom Economy)*** – An efficient chemical process ensures that the maximum amount of starting materials is used in the final product so that no atom is wasted.

(5) ***Taking Advantage of Chemicals Designed for Degradation*** – Reduce the effect on the environment by using chemicals that are designed to be biodegradable.

(6) ***Establishment of In Process Controls for Pollution Prevention*** – To avoid [illegible] substances, adopt real-time analysis and in process monitoring d[illegible] synthesis.

(7) ***Use of Renewable Feedstocks*** – Use raw materials or renewable feedstocks (waste from other proce[illegible] products derived from agricultural streams) whenever technically [illegible].

(8) ***Encourage Energy Efficiency*** – The realization of the economical and en[illegible] a chemical process and the development of alternative means to reduc[illegible]

SOCIETY, TECHNOLOGY AND SCIENCE

RADIATION POLLUTION

[illegible]

Sources of radioactive pollution and its effects

(i) Radioactive Cloud [illegible]

(ii) Energy [illegible] destroyed

(iii) Tumors: People [illegible]

(iv) Radioactive Elements [illegible] affects our so[illegible] and anima[illegible]

(v) Nuclear Explosions [illegible] which are operated in sea make sea water po[illegible] aquatic life

(vi) Gamma radiations

- Among the radioa[illegible] gamma radiations are the most dangerous since [illegible] energy and big penetrating power
- These [illegible] therefore pass freely in the human body where they lose ene[illegible] destroy the [illegible] cells by converting them into charged particles ions. These charged [illegible] chemically very reactive and hence disturb cell membrane. Hence it reduces the e[illegible] enzymes and even damage genes and chromosomes
- All this results in diseases like leakaemania and cancer

(vii) Nuclear Radiations: In a nuclear reactor, U-235 is used as a nuclear fuel. It undergoes n[illegible] energy is produced. Nuclear radiations are produced in the processes like mining and enrichment [illegible] taking place in the nuclear reactor. These radiations can leak from the reactor and therefore [illegible] health of the human beings and animals

Control measures for minimizing radioactive pollution

Disposal of Nuclear Waste

The waste material produced in the mining, enrichment and fission of U 235 inside the rector a[illegible] called nuclear wastes

At present most of the nuclear wastes are being sorted in strong leak proof containers. These wi[illegible] be dispos[illegible] whenever a safe method of their disposal is found out

Using catalytic Converters

A catalytic converter removes pollutant gases from the exhaust by oxidizing or reducing them

- The exhaust gases pass through a converter containing a precious metal catalyst, usua[illegible] platinum and rhodium
- Several reactions may take place
- NO_x and CO may take part in a redox reaction which neatly removes both of them at the same time
- NO_x oxidizes CO to CO_2 and is reduced to harmless nitrogen gas

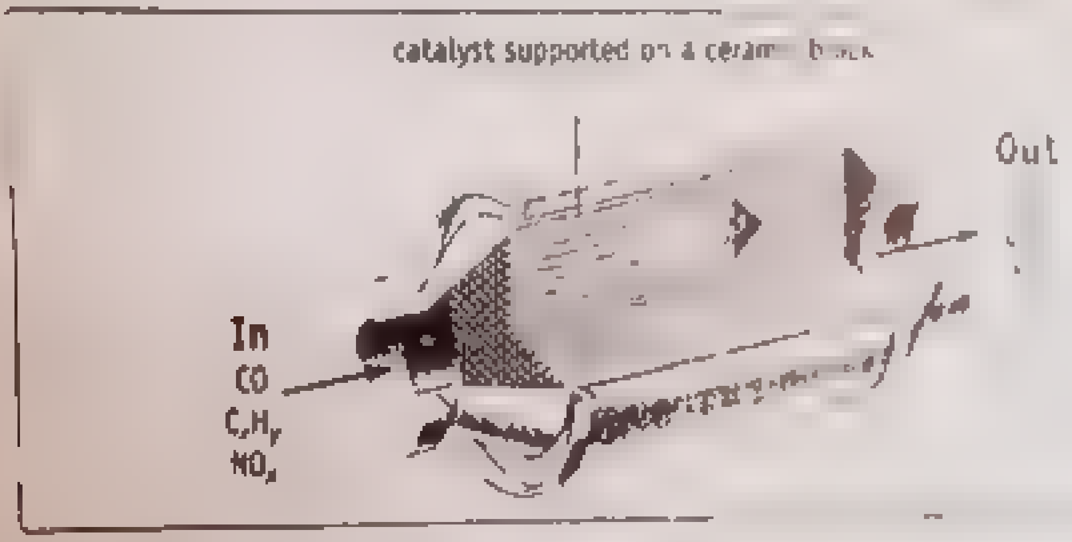
$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

- CO and C_xH_y are oxidized by air

$$2CO + O_2 \rightarrow 2CO_2$$

e.g. $C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

- For all three of these reactions happen, it is necessary to use a ... in order and ... have an oxygen monitor fitted to the engine.
- This checks the quantity of oxygen going into the engine to make sure there is enough to carry out the oxidation reactions.
- The overall result of passing exhaust gases through this kind of catalyst system is to convert CO, NO_x and C_xH_y to relatively harmless N_2, CO_2 and H_2O.
- The catalytic reactions do not start working until the catalyst ... of about 200 C so they are not effective until the engine has warmed up.
- Catalyst systems of this type cost several hundred pounds. It is mainly ... high cost ... precious metal they contain. The catalyst is poisoned by lead so unleaded ... be used.



WATER POLLUTION

The waste water from household and industries without treatment to river is dangerous

Sources:

- It comes from places like factories, farms and industry.
- Waste water from manufacturing or chemical processes in industries ...
- Industrial waste water usually contains specific and readily ... many cases the pollution in our rivers comes from our homes.
- Incorrect plumbing could mean that waste water from dishwashers ... even toilets.
- Other impurities includes organic materials and plant nutrients ...
- The main organic materials are food and vegetable ... washing powders, etc.
- These flushed directly into a local river. These 'misconnected' ... rivers and streams, especially in towns and cities.
- Today many people dump their garbage into streams, lakes, rivers ... becomes the final resting place of cans, bottles, plastics and other ...
- The various substances used for keeping our h... chemicals.

Types of Drainage Systems

There are normally two forms of drainage ... waste water ...

(i) Surface water drains, or storm drains

These carry rainwater from road surfaces and ... untreated

(ii) Foul water drains

These carry waste water from toilets, sinks, baths and household appliances to the sewage ... This water is treated before it can safely flow back into river and streams

Pollution in America

- Americans generate 1.6 million tons of household hazardous waste per year
- The average home can accumulate as much as 100 pounds of household hazardous ... basement or garage and in storage closets. When improperly disposed of, household hazardous ... can create a risk to people and the environment
- Paints, cleaners, oils, batteries, and pesticides are examples of just a few of the common ... hazardous wastes that need special disposal

Eutrophication

When fresh water is artificially supplemented with nutrients, it results in an abnormal increase in the ... of water plants. This is known as eutrophication

- The discharge of waste from industries, agriculture, and urban communities into water bodies ... stretches the biological capacities of aquatic systems
- Chemical run-off from fields also adds nutrients to water
- Excess nutrients cause the water body to become choked with organic substances and organisms
- When organic matter exceeds the capacity of the micro organisms in water that break down ... the organic matter, it encourages rapid growth of algae
- When the algae die, their remains add to the organic wastes already in the water, eventually ... becomes deficient in oxygen
- Anaerobic organisms (those that do not require oxygen to live) then attack the organic wastes ... gases such as methane and hydrogen sulphide. These are harmful to the oxygen-requiring ... forms of life. The result is a foul-smelling, waste-filled body of water
- Untreated sewage effluent in the water causes oxygen levels to drop drastically. The sewage ... covers the bed of the watercourse like a blanket. In more severe cases the river can no longer support fish, insects and animals that live in and around the water

Effects of Polluted Water

- Polluted water is unsuitable for drinking, recreation, agriculture, and industry
- It diminishes the aesthetic quality of lakes and rivers
- More seriously, contaminated water destroys aquatic life and reduces its reproductive ability
- Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution
- Once an aquifer is contaminated, it may be unusable for decades. The residence time can be anywhere from two weeks or 10 000 years

AIR POLLUTION

The Biggest Source of Air Pollution:

- The biggest source of air pollution is automobiles
- In past there was bull cart, donkey carts animals were used by
- Now-a-days Aeroplane cars, buses and trains are used for transportations. These vehicles need energy for their working in the formal petrol or gas to provide energy for motion of vehicle
- The end product of this burning include energy plus different gasses include hydrocarbons, Nitrogen oxides carbon monoxide, Benzene sulphur heavy metals and particles. These gases enter into air and pollute in when human breath in such polluted environment it causes asthma, coughing nausea chest pain, bronchitis diseases etc

Effects of Air Pollution

- It is estimated that usually 24000 deaths occur due to air pollution because pollution damage central Nervous System
- Automobiles are responsible for depletion of ozone in stratosphere shell because of source of CFCs entering the atmosphere which is escape from vehicle air condition ACs
- Vehicles are responsible
  - ✓ for 80% pollution in metropolitan region
  - ✓ three fold increases in energy consumption for global warming. It is because burning of fuel produces CO_2

Control of Air Pollution

(i) Ways to improve the impact of cars

Ways to improve impacts of car like uses of small cars cleaner cars efficient engine catalytic converters are compulsory and use of biocheral. The following measures may be helpful

(a) Use of Fuel cells It cause only water comes out as its exhaust element vehicle pose problem because of range of batteries and seep

(b) Use of Hybrid electric petrol It cut down the fuel wastage and electric energy on board e.g. In Delhi they demolished the buses run on diesel

(c) Restricts the occurs to the cities or part of cities

e.g. Chester York, oxford have given free space for parking at the edge of town

(d) Improve information about road condition and public transport

e.g. Zurich zone referendum given the priority to tams trolleys, buses parking provides for 50% of all the trips as by means of public transport

(e) Polluter pay

It is another solution where the pollution emitted by the car is and the price is changed on the buses of level multiplies the distance travel

(ii) Technological improvements

Several technological innovations have been made from 1970 onwards in engine technology. Technological improvements include

- Technological changes to reduce cooling zone of engine wall and reduce carbon monoxide emission.
- Computer control at IC engine
- Catalytic converter technology (CCT) emission
- Trap oxidizers ad ceramic filter an Diesel vehicles
- Direct injection fuel efficient Diesel

OZONE

Occurance

- Ozone layer is found in the stratosphere approximately ...
- Ozone molecules have three atoms of oxygen instead of ...

Advantage

- The ozone layer protects us from the harmful effects of ... coming from the sun, socially UVB
- Any significant decrease in ozone in the atmosphere would result in ... reaching the earth surface
- Increase in levels of UVB radiation can result in the increase ... eye disorder including catavart and effect plants animals and plastic ...

Ozone depletion

- In 1985 scientists discovered that there is severe ozone depletion in the A... confirmed by American Satellite observations
- Chlorofluorocarbons (CFCs) were invented in 1928 found many used ... conditioners, solvent, five extinguishers etc these CFCs are ... stratosphere and cause ozone depletion This has been dramatically ... hole
- The United Nations Environment Programme (UNEP) has been addressing the ... ozone layer since 1977 and in 1981 UNEP's Governing Council set up a ... global framework conventions for protection of ozone layer
- By reducing the use of CFCs we can protect ozone layer for ...
- Montreal protocol on substances the deplete the ozone layer was finally agreed ... 1987 and adopted by the Government in this protocol ozone depleting substances ...

Alternatives to ozone-depleting halocarbons

- Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are alternative ...
- These are being used to replace ODS in industrial and commercial ... more widespread
- Other alternatives to ODS include ammonia, carbon dioxide and hydrocarbons

The relationship between ozone-depleting substances and their halocarbon alternatives ... warming

- Ozone depleting substances (ODS) and their halocarbon alternatives have ... potential and contribute to climate change
- The production of some ozone depleting substances (e.g. CFCs) has been ... emission reductions of ozone-depleting substances into the atmosphere
- However emissions of other ODS (e.g. hydrochlorofluorocarbons (HCFCs) ...) hydrofluorocarbons (HFCs) is expected to continue to increase
- HFCs are ODS refrigerants alternatives and their use is becoming more widespread
- Although HFCs have no ozone-depletion potential they do have high global ... thousands of times more potent greenhouse gases than carbon dioxide
- Regulations that prevent or minimize ODS and other halocarbons emissions serve a ... benefit of lowering emissions that destroy the ozone layer and contribute to climate ...

Are ozone-depleting substances still an important environmental concern?

Although the production and use of [illegible] emissions continues to be an important [illegible] stratospheric ozone layer causes increased health risks and environmental impacts, such as cataracts, skin cancer and climate change.

NATURAL WATER PURIFICATION METHODS

There are several, natural ways that you can p[illegible] water.

- ***In the event of an emergency it may become necessary to purify the water for drinking in order to avoid getting sick.***
- ***Though many people think purifying water is difficult. However, there are a number of simple natural means of purifying water that can easily be used in an emergency.***

SAND

- One of the most common ways that w[illegible] passing it through sand and soil.
- If contaminated water (say urine) is [illegible] water is going to travel down until it reaches the saturation level.
- The other chemicals that are mixed with [illegible] sand until only the water is left.

  This method of water purification is used in many sewage tre[illegible] as a big part of separating water out of the waste that goes through the plant.

BOILING

- Water can be boiled to make it more pure.
- Boiling water kills bacteria and other germs in the water [illegible]
- ***Procedure***
  - ✓ Water is poured into a sealed pot, with a tube leading out of it.
  - ✓ The water turns into steam, and the steam escapes through the tube.
  - ✓ The tube transports the steam to another container where the steam condenses back into water.
  - ✓ This process can eliminate more contaminants [illegible] as [illegible] but it is also more complicated.

CLOTH FILTRATION

- Cloth filters can be used to help keep larger contaminants out of water.
- **Procedure:**
  - ✓ This process is very simple.
  - ✓ Pour the water through a cloth, or through several layers of cloth.
  - ✓ The cloths' weave will strain the water and hold back impurities.
  - ✓ This is the same process that happens when a coffee filter is used, except that the filter is paper rather than cloth.
  - ✓ Paper can work as well.
  - ✓ The coffee filters or similar devices may be used instead of a clean [illegible]

How rain water seepage through hazardous waste dumpsites can dissolve in drinking water supplies

Hazardous waste:

Hazardous waste is waste that is dangerous or potentially harmful to our health or the environment.

- Hazardous wastes can be liquids, solids, gases, or sludges
- They can be discarded commercial products like cleaning fluids or pesticides or the by-products of manufacturing processes
- It is very important to dispose off hazardous waste carefully otherwise it contaminate the air, water and soil.

Groundwater:

Groundwater is rain water or water from surface water bodies, like lakes or streams that soaks into the bedrock. It is stored underground in the tiny spaces between rocks and particles of soil.

Groundwater contaminants come from two categories of sources

Point sources

These are Landfills, leaking gasoline storage tanks, leaking septic tanks and accidental spills

Non-point sources

Infiltration from farm land treated with pesticides and fertilizers is an example of a non point source

- Among the more significant point sources are municipal landfills and industrial waste disposal sites. If either of these occur in or near sand and gravel aquifers, the potential for widespread contamination is greatest
- Leaks of petroleum products have been increasing over the last two decades. It is because underground storage tanks installed in large numbers in the 1950s and 1960s have become corroded. Before 1980 most underground tanks were made of steel. Without adequate corrosion protection, up to half of them leak by the time they are 15 years old.
- Groundwater dissolves many different compounds. Most of these substances have the potential to contaminate large quantities of water e.g., one litre of gasoline can contaminate 1 000 000 litres of groundwater. This problem is particularly severe in the Atlantic provinces where there is a high ... consumers start tasting or smelling gasoline. In many cases, the problem is noticed long after the aquifer is contaminated e.g. ...
- Groundwater can become contaminated in many ways. Chemicals from hazardous wastes ... unsecured landfills. If rain water or surface water comes into contact with contaminated soil while seeping into the ground, it can become polluted and can carry the pollution from the soil to the groundwater. contaminants can also spread to wells or surface water making it unsafe to drink
- Groundwater can also become contaminated when liquid hazardous substances themselves soak through the soil or rock into the groundwater. Some liquid hazardous substances do not mix with groundwater but remain pooled within the soil or bedrock. These pooled substances can act as long-term sources of groundwater contamination as the groundwater flows through the soil or rock and comes into contact with them
- *Groundwater contamination is extremely difficult, and sometimes impossible to clean up*
- Apart from chemical pollutants the major culprits are Bacteria and Viruses which cause most commonly found water borne diseases.

Bacterial diseases. Gastro-enteritis, Typhoid, Cholera, Paratyphoid, Dysentery and Diarrhea

Viral diseases. Polio, Dysentery, Gastro-enteritis, Diarrhea and Jaundice, Hepatitis

REPLACING CFCs

- Few compounds have CFCs combination of non-flammability, non-toxicity and inertness. For uses such as refrigeration and aerosols it is necessary to find compounds with exactly the right boiling point.
- ***Hydrofluorocarbon (HFCs).***
  Some of the important replacements for these uses are the hydrofluorocarbons. CFCs also known as hydrofluorocarbon or HFCs.) An example is 1,1,1,2-tetrafluoroethane CH_3CH_2F, which is used as a refrigerant.
- ***HFCs are comparatively safe.***
  - ✓ HFCs have the advantage that they contain no Cl atoms, so they do not release damaging Cl radicals in the stratosphere.
  - ✓ Moreover, their molecules include C-H bonds, which are relatively reactive. It means that these compounds break down in the atmosphere more quickly than CFCs so they do not persist for so long.

KEY POINTS

- A [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible]
- [illegible] nitrogen is favorably oxidized to NO, N[illegible]
- By keeping the vehicle prop[illegible] pollution caused by CO and hydrocarbons present in the [illegible]
- [illegible]
- [illegible]
- [illegible] entration. Marine animals an[illegible] [illegible] damages the feather of the birds [illegible] als and sometimes causes their death
- Surfactants are organic compounds having polar or hydrophilic groups such as –COOH, $-SO_3H$, N[illegible] or non-polar or lyophilic groups soluble in water
- The waste heat from electrical generating stations is transferred to cooling water obtained from loc[illegible] water bodies such as a river, lake or ocean
- Water purification is a process of removing harmful substances and odor from a raw water source

EXERCISE

Q1: Select the right answer from the choices given with each question.

(i) Air is polluted by:
(a) Toxic materials (b) Hydrocarbons (c) Harmful gases (d) All of above

(ii) Which of following gas is not pollution?
(a) SO_2 (b) CO (c) CO_2 (d) NO

(iii) Oxides of sulfur and nitrogen react with oxygen to form:
(a) Bases (b) Acids (c) Salts (d) All of above

(iv) Oxidizing smog consists of high concentration of
(a) SO_2 (b) Ozone (c) NO_2 (d) Cl_2

(v) Thickness of ozone is
(a) 20-25 kM (b) 25-28km (c) 30-32km (d) 20-30km

(vi) Ozone is destroyed by:
(a) SO_2 (b) NO_2 (c) Chlorofluorocarbons (d) None of above

(vii) In leather industry:
(a) Chromium (VI) is used (b) Chromium (III) is used (c) Nickel is used (d) Aluminum is used

(viii) Water is purified:
(a) Aeration (b) Coagulation (c) Disinfection (d) All of above

(ix) The Ecosystem is the smaller unit of:
(a) Biosphere (b) Lithosphere (c) Atmosphere (d) Hydrosphere

(x) When chlorine is passed through water then the disinfection is done due to the production?
(a) HCl (b) HOCl (c) NOCl (d) $HClO_3$

(xi) Peroxyacetylnitrate (PAN) is an irritant to human beings and it affects
(a) eyes (b) ears (c) stomach (d) nose

(xii) Fungicides are the pesticides which
(a) control the growth of fungus (b) kill insects (c) kill plants (d) [illegible]

ANSWERS TO MULTPLE CHOICE QUESTIONS

(i) Ans: (d) All of above	**(ii) Ans: (c) CO_2**
Air is polluted by toxic materials like PAN, hydrocarbons and gases like SO_2 etc	CO_2 is generally not considered as pollution [illegible] by plants for photosynthesis
(iii) Ans: (b) Acids	**(iv) Ans: (b) Ozone**
This is the cause of acid rain	[illegible]
(v) Ans: (b) 25-28km	**(vi) Ans: (c) Chlorofluorocarbons**
The thickness of ozone in stratosphere is 25-28 km	[illegible]
(vii) Ans: (a) Chromium (VI) is used	**(viii) Ans: (d) All of above**
Chromium (VI) is used in leather industry	[illegible]
(ix) Ans: (a) Biosphere	**(x) Ans: (b) HOCl**
In ecosystem both living and non-living environment is present so it is a biosphere	[illegible]
(xi) Ans: (a) eyes	**(xii) Ans: (a) control the growth of fungus**
PAN causes irritation in eyes	[illegible]

Q2: Give brief answers for the following questions.

(i) What are components of environment?
(a) Atmosphere (b) Hydrosphere
(c) Lithosphere (d) Biosphere

(ii) Briefly discuss the role of atmosphere in our environment?
Our surrounding on earth is called atmosphere are [illegible]

(a) These gases absorb harmful radia... and electromagnetic radiatio... life on earth. Otherwise these rays are very harm... to living things on earth

(b) N_2 is used by nitrogen fixing bacteria

(c) O_2 is necessary for breathing ...

(d) CO_2 is necessary for pho...

(e) Water vapours are respon...

(iii) Enlist different layers of our atmosphere

Atmosphere has been divided into f...

1 Troposphere 2 Stratosphere 3 Mesosphere 4 Thermosphere

(iv) What are sources of air pollution?

Sources of air pollution are

(a) Nitrogen oxides (NO and NO_2

(b) Oxides of sulphur (SO_2 and SO_3)

(c) Volatile organic compounds (VOCs)

(d) Carbon monoxide (CO)

(v) What are the important air pollutants?

Important air pollutants are

(a) Nitrogen oxides

(b) Sulpher oxides

(c) Peroxyacetyl nitrates

(d) Peroxybenzol

(e) Volatile organic compounds

(f) Carbon monoxide

(vi) What are the sources of CO emission? Discuss its effects

Source of CO

- Incomplete combustion of carbon containing fuels (CO
- Incomplete combustion of agricultural of slush matter (CO)
- During the reaction in blast furnace (CO)
- Cigarette smoke (CO)

Effects

- Causes Anoxia (Oxygen Starvation) result suffocation
- Causes Green house and Global Warming results climatic changes
- Causes Acid rain
- Causes Acid rain
- Respiratory irritation

(vii) Differentiate between (i) industrial and photochemical smog (ii) Primary and secondary pollutants.

a. Industrial smog

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can com... with fog to create industrial smog

b. Photochemical smog

It is a condition that develops when *primary pollutants* (oxides of nitrogen and volatile ... compounds created from fossil fuel combustion) interact under the influence of sunlight to p... mixture of hundreds of different and hazardous chemicals known as *secondary pollutants*

Primary Pollutants

The pollutants which directly comes into the atmosphere from the source are called primary pollutants.

e.g. oxides of nitrogen and volatile organic compounds (VOCs) created from fossil fuel combustion etc

Secondary Pollutants

The pollutants which are derived from primary pollutants by chemical reactions in the atmosphere are called secondary pollutants

e.g. sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid, peroxyacetyl nitrate PAN

(viii) How does photochemical smog differ from reducing smog?

Photochemical smog is a condition that develops when *primary pollutants* oxides of nitrogen and volatile organic compounds created from fossil fuel combustion interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as *secondary pollutants*. While reducing smog is formed when smoke and sulphur dioxide produced from burning of coal combine with fog.

(ix) What is global warming?

When sunlight consists of ultraviolet rays, visible light and infrared rays falls on the top of the atmosphere the harmful ultra violets rays are absorbed by O_3 layer and hence do not reach on the other hands, the visible light and infrared rays pass through the CO_2 layer and falls on the earth. Since the infrared radiations have heating effect they heat the earth and its objects. This is called global warming.

(x) What are the latest predictions about global warming?

- If the atmosphere contains too much quantity of CO_2 the green house effect is considerably increased.
- Thus due to excess quantity of CO_2 present in the atmosphere the temperature of the earth is increased too much. This too much high temperature melts all the glaciers snow mountains, floods the low-lying areas of the earth.
- It also changes the biological Activity of oceans and the patterns of cropping etc.

(xi) What gases are responsible for green house effects?

The gases are

(a) CO_2 and CO (b) Methane (c) CFCs (d) Nitrogen oxides

(xii) Briefly discuss effects of acid rain.

(i) It makes the lakes so acidic that they can no longer support fish life.
(ii) The yield of agricultural crops is also reduced.
(iii) HNO_3 acid rain gradually eats up lime stone and marble of the buildings and corrodes metals.
(iv) It fades the color of fabrics (e.g. cotton, nylon and rayon) leather and paper.
(v) Causes extensive leaf drop in plants.
(vi) It is very corrosive and attacks skin.
(vii) Acidification of soil and rocks can leach metals like Al, Hg, Pb and Ca and discharge them into water bodies. It also damages steel, paint, plastic, cement, masonry work and sculptural monuments.

(xiii) What are sources and environmental effects of? (a) VOCs (b) PAN

Page 462 given In Table

(xiv) What are effects of excess of CO_2 present in atmosphere?

- If the atmosphere contains too much quantity of CO_2, the green house effect is considerably increased.
- Thus, due to excess quantity of CO_2 present in the atmosphere the temperature of the earth is increased too much. This too much high temperature melts all the glaciers snow mountains, floods the low-lying areas of the earth.
- It also changes the biological Activity of oceans and the patterns of cropping etc.

(xv) Discuss the sources and typical effects of SO_2 as pollutant

Page 462 given in Table

(xvi) Briefly discuss the sources and typical effects of oxides of nitrogen

Page 462 given In Table

(xvii) What is ozone? How does it work as safeguard?

The ozone (O_3) is the protective [illegible] The thickest layer of O_3 exists at a height of [illegible] ultraviolet radiations coming from the sun. Thus it saves the [illegible]

(xviii) How ozone is formed in stratosphere?

O_3 is produced in the upper part of the atmosphere [illegible]

$$3O_2 \rightarrow 2O_3$$

[illegible]

(xix) What do you know about "Ozone hole"?

In 1985, scientists discovered that there is severe ozone d[illegible] chlorofluorocarbons reach stratosphere and cause ozone [illegible] through Antarctic ozone hole

(xx) How is ozone layer depleting?

i) oxides of nitrogen in the atmosphere converts O_3 into O_2

$NO + O_3 \rightarrow NO_2 + O_2$

$NO + O \rightarrow NO_2$

Nuclear tests generate high temperature. Due to this the nitrogen is [illegible] ozone layer

ii) Use of chloro-flouro carbons destroy ozone layer by decomposing O_3 into O_2

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O_3 \rightarrow Cl + 2O_2$

(xxi) What are the effects of ozone layer depletion?

If O_3 layer in the atmosphere disappears completely, then all the harmful ultra[illegible] from the sun would reach the earth. It would cause skin cancer in men and animals [illegible] the plants. Hence. All the life on earth would then gradually be destroyed

(xxii) What should we do to save ozone?

In order to save the destruction of O_3 layer by fluoro-chloro carbons, their use should be [illegible] Some new types of substances should be discovered which may be used as aerosol spray [illegible] should not react with O_3 layer

Leaded petrol should be used in automobiles

(xxiii) What is water pollution? Write different types of water pollution?

The contamination of water with the substances which have adverse effects on human be[illegible] plants is called water pollution

Sources of water pollution are

- Oil spillage
- Live-stock waste
- Industrial waste
- Leather tanneries

(xxiv) Briefly discuss the effects of water pollution.

- Polluted water is unsuitable for drinking, recreation, agriculture and industry
- It diminishes the aesthetic quality of lakes and rivers.
- The contaminated water destroys aquatic life and reduces its reproductive ability
- The polluted water causes several diseases

(xx) How preliminary treatment of waste water is done?

In Preliminary treatment most of the suspended particles are removed which are visible

(xxi) What is primary treatment of waste water?

Primary treatment involves the removal of sand particles are other particles which are visible

(xxii) What is secondary treatment of waste water?

Secondary treatment involves:

- Solids removal
- Oils and greases
- Soft organics
- Hard organics
- Acid and alkalis
- Toxic materials

(xxiii) How would avoid from thermal pollution?

The companies use hot water in cooling their generators. When hot water is released in water bodies, it decreases the solubility of dissolved oxygen. Thus cause serious threat to life in water. So the companies should decrease the temperature of hot water before discharging into water bodies.

Q3: Give detailed answers for the following questions.

(i) Describe different chemical reaction occurring in our atmosphere

Page 461

(ii) Write a comprehensive note on acid rain.

Page 465

(iii) How would you control air pollution? Describe different methods.

Page 467

(iv) What is Thermal Pollution? Discuss its sources and environmental effects.

Page 473

(v) What is waste water treatment? Discuss different methods of it.

Page 474

(vi) Write a note on Green Chemistry.

Page 478

TEST YOUR SKILLS **Marks: 85**

OBJECTIVE

Time 20 Minutes **Marks 17**

Note

Q1 Circle the correct option i.e A B C (D) Each part carries one mark

a by plants for photos b by nitrogen fixing bacteria

An example of primary p

a Oxides of nitroge

c) d both a & b

Bronchial constriction

iv) Which of the fol

(a) SO_2 b NO_2 (c) CO (d) All

a A b Al, Hg, Pb, Ca

(vi) The thickest layer O_3

(a) 23 km (b) 2.3 km (c) 23m (d) 2

vii) Which of following gas is not pollution?

(a) SO_2 (b) CO (c) CO_2 (d)

(viii) Oxidizing smog consist of high concentrat

a SO_2 (b) ozone (c) NO_2 (d)

+4 (b) +6 (c) +5 (d) +2

(x) The Ecosystem is the smallest unit of

(a) Biosphere

a) HCl (b) HOCl (c) NOCl (d)

Water is purifi

a) Aeration (b) Coagulation (c) Disinfection (d) All

Which of the

(a) Po

COOH polar or hydrophi

xvi) One liter of (c) NH_4^+ (d) all

Lakes of groundwater

(c) 1000000 (d) 10000

disease?

(a) Jaundice T d paratyphoid

xviii) Which non – metallic elements are generally resistant to biological processes unless very d ?

(a) Arsenic (b) selenium (c) both a & b d None

(II) Time: 2 35 Hours (I) SUBJECTIVE

Total Marks Section B and C 68

(ii) Section – B (Marks 42, (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines

i (a) What are environment?

b Write layers of atmosphere (02)

a Difference primary & secondary pollutants? (01)

(b What is smog (02)

What are sources of organic compounds VOCs in atmosphere? (01)

iv) Which conditions occur to begin the chemical process of photochemical smog development? (03)

a) PAN stands for (03)

b What is acid rain (01)

What are different sources & environment effects of? (02)

VOCs PAN (03)

How O_3 is decomposed by oxides of nitrogen?

a How ozone is produced? (03)

(02)

(b) Enlist the possible alternatives of the use of CFCs (01)

(ix) (a) Which diseases are caused by live stock? (1.5)

(b) What is swamp? (1.5)

(x) (a) What is green Chemistry? (02)

(b) What is synthetic efficiency? (01)

(xi) Give principles of green chemistry (03)

(xii) (a) How would you avoid from thermal pollution? (02)

(b) Give two examples of fluoro – chloro carbons? (01)

(xiii) What is secondary treatment of waste water? (1.5)

(b) What is primary treatment of water? (1.5)

(xiv) Briefly discuss the effect of water pollution. (03)

(xv) (a) What is global warming? (1.5)

(b) Which factors are playing major role in global warming? (1.5)

(xvi) Discuss the sources & typical effects of oxides of S as pollutant (03)

(xvii)(a) What are the latest predictions about global warming? (02)

(b) What gases are responsible for greenhouse effect? (01)

(xviii) What are the effects of ozone layer depletion? (03)

(xix)(a) What are the important air pollutants? (1.5)

(b) What should we do to save ozone? (1.5)

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

1 (a) What are the effects of acid rain? (04)

(b) Is CO_2 responsible for green house effect? If yes then How? (04)

(c) How we can control the air pollution caused by hydrocarbons & CO? (05)

2 (a) What is radioactive pollution? What are sources of radioactive pollution & [illegible] [illegible]

(b) What are control measures for minimizing radioactive pollution? (04)

(c) Write tow salient principles of green chemistry (04)

3. (a) What are different treatments of industrial wastewater? (05)

(b) How following parameters help up to determine the quality of water? (04)

i) BOD ii) COD

(c) What are suspended solid & sediments? How they are caused? (04)

CHAPTER # 24
ANALYTICAL CHEMISTRY

Analytical Chemistry

Analytical chemistry is the branch of chemistry that deals with separation and analysis of its components

The separation is carried out before qualitative and quantitative analysis.

Qualitative analysis

Qualitative analysis provides the identity of a substance (composition of chemical species

Quantitative analysis

Quantitative analysis determines the amount of each components present in the sample

Scope of Analytical Chemistry

In analytical chemistry different techniques and instruments used for analysis are studied. This branch covers food, water, environmental and clinical analysis.

CLASSICAL METHOD OF ANALYSIS

Exercise Q3 (i), What is combustion analysis? Describe its different steps

Combustion Analysis and determination of Molecular Formula

The experimental technique by which amount of various elements present in a substance are ... combustion is called combustion analysis

- Empirical and molecular formulas for compounds that contain only carbon and hydrogen, carbon, hydrogen and oxygen ($C_xH_yO_z$) can be determined by combustion analysis.
- The only products will be CO_2 and H_2O and these two products of combustion are separated ...

Procedure

The steps for this procedure are

- Weigh a sample of the compound to be analyzed and place it in the apparatus shown below.
- Burn the compound completely. The only products of the combustion of a compound that contains carbon and hydrogen (C_xH_y) or carbon, hydrogen and oxygen ($C_xH_yO_z$) are carbon dioxide and water.
- The H_2O and CO_2 are drawn through two tubes. One tube contains a substance that absorbs water and the other contains a substance that absorbs carbon dioxide.
- Weigh each of these tubes before and after the combustion. The increase in mass in the first tube is the mass of H_2O that formed in the combustion, and the increase in mass for the second tube is the mass of CO_2 formed.
- Assume that all the carbon in the compound has been converted to CO_2 and trapped in the second tube. Calculate the mass of carbon in the compound from the mass of carbon in the measured mass of CO_2 formed.
- Assume that all the hydrogen in the compound has been converted to H_2O and trapped in the first tube. Calculate the mass of hydrogen in the compound from the mass of hydrogen in the measured mass of water.

- If the compound contains oxygen as well ... subtracting the mass of carbon and hyd... mass of the oxyge... ample of compound
- Use this data to determine the empirical and molecu...

Fig. Apparatus for Combustion Analysis

Example

Consider a substance called trioxane. Formaldehyde, CH_2O, is unstable as a ... mixture of a substance called trioxane ... dissolved in a solvent, like water, before ...

The molec... the data from two different experiments.

(i) In the first exper... and 25.612 g CO_2 are formed.

(ii) In the second experiment, the molecular mass of trioxane is found to be 90.0...

Calculations

We can get the molecular formula of a compound from ... the empirical formula, we need to determine the mass in grams of ... 17.471 g of trioxane. Thus, we need to perform these general steps.

- ***Step-I:*** Determine the grams of carbon, hydrogen, and oxygen from the given data.
- ***Step-II:*** Determine the emp... from the grams of carbon, hydrogen, and ox...
- ***Step-III:*** Determine the molecular form... molecular mass.

Step-I

Since it is assumed that all the ... carbon in 17.471 g trioxane is determined by calculating the mass ...

$$?\,g\,C = 25.612\,g\,CO_2\left(\frac{1\,mol\,CO_2}{44.010\,g\,CO_2}\right)\left(\frac{1\,mol\,C}{1\,mol\,CO_2}\right)\left(\frac{12.011\,g\,C}{1\,mol\,C}\right) = 6.9899\,g\,C$$

Since it is assumed that all the hydrogen ... 17.471 g trioxane is determined by calculating the ...

$$?\,g\,H = 10.477\,g\,H_2O\left(\frac{1\,mol\,H_2O}{18.0153\,g\,H_2O}\right)\left(\frac{2\,mol\,H}{1\,mol\,H_2O}\right)\left(\frac{1.00797\,g\,H}{1\,mol\,H}\right) = 1.1724\,g\,H$$

Since trioxane contains only carbon, hydrogen and oxygen, ... subtracting the masses of carbon and hydrogen from the total mass of trioxane.

$$?\,g\,O = 17.471\,g\,trioxane - 6.9899\,g\,C - 1.1724\,g\,H = 9.309\,g\,O$$

Step-II

We now calculate the empirical formula

$? \text{ mol C} = 6.9899 \text{ g C}\left(\frac{1 \text{ mol C}}{12.011 \text{ g C}}\right) = 0.58196 \text{ mol C} \div 0.5818 \cong 1 \text{ mol C}$

$? \text{ mol H} = 1.1724 \text{ g H}\left(\frac{1 \text{ mol H}}{1.00797 \text{ g H}}\right) = 1.1631 \text{ mol H} \div 0.5818 \cong 2 \text{ mol H}$

$? \text{ mol O} = 9.309 \text{ g O}\left(\frac{1 \text{ mol O}}{15.9994 \text{ g O}}\right) = 0.5818 \text{ mol O} \div 0.5818 = 1 \text{ mol O}$

Step-III

The empirical formula is CH_2O, which can be used to calculate the molecular formula

Empirical formula mass = 1(12.011) + 2(1.00794) + 1(15.9994)
= 30.026

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079}{30.026} \cong 3$$

Molecular formula $C_3H_6O_3$

Drawbacks

The classical method i.e. combustion analysis is only limited to those organic compounds which carbon, hydrogen and oxygen. So there is a need of such methods which explain/find atoms/elements present in an organic compounds. Hence now modern methods are used for this purpose

QUICK QUIZ-1

(1) Give difference between qualitative and quantitative analysis

Qualitative analysis provides the identity of a substance (composition of chemical species)
Quantitative analysis determines the amount of each components present in the sample

(2) Name the products obtained by complete combustion of hydrocarbon

The only products of the combustion of a hydrocarbon are carbon dioxide and water

e.g. $CH_4 + 2O_2 \rightarrow 2CO_2 + 2H_2O$

(3) How mass of oxygen is calculated if it also present along with carbon and hydrogen

If the compound contains oxygen as well as carbon and hydrogen, then the mass of the oxygen is calculated by subtracting the mass of carbon and hydrogen from the total mass of the organic sample of compound

(4) Give general steps used to calculate empirical formula

(i) Determine the percentage composition of each element in a substance
(ii) Divide the percentage of each element by its atomic mass to get number of gram atoms/moles
(iii) Divide the moles of each element by the smallest number of moles to get atomic ratios
(iv) If atomic ratios are not in simple whole number, then multiply with a small suitable number ... number ratio

Thus empirical formula is obtained

(5) Give drawback of combustion analysis

The classical method i.e. combustion analysis is only limited to those organic compounds ... carbon, hydrogen and oxygen

[M]ODERN METHODS OF ANALYSIS

- Modern chemistry laboratories [illegible]
- These instruments are [illegible] work on
- Laboratories [illegible] very expensive [illegible]

[SP]ECTROSCOPY

[Sp]ectroscopy:

Spectroscopy [illegible] information about the [illegible]

[Sp]ectroscope:

A spectroscope is [illegible] changes.

[Th]eory

When electromagnetic radiation such as [illegible] infrared shines on a chemical [illegible] interact with the radiation [illegible] commonest example [illegible] when chemicals emit or absorb [illegible] particular frequency. The [illegible] chemical interacts with radiation [illegible] molecules and structure.

Different kinds of radiation interact [illegible] in different ways as shown in the figure [illegible] The effects are given in the table.

[Ty]pes of Spectroscopy

There are many types of spectroscopy [illegible] [th]ese five types of spectroscopy are [illegible] chemists.

These are: infrared, ultraviolet-visible, nuclear magnetic [illegible] spectroscopy and mass spectroscopy.

Table

[Ho]w different types of radiation interact with chemicals

Type of radiation	Frequency range /Hz	Effect on molecule	[illegible]
[ul]traviolet	$10^{15}-10^{17}$	excites the electrons	[illegible]
[vi]sible light	$10^{14}-10^{15}$	excites the electrons	[illegible]
[in]frared	$10^{11}-10^{12}$	makes bonds vibrate	[illegible]
[mi]crowaves	$10^{9}-10^{11}$	makes molecules rotate	[illegible]
[ra]dio waves	$10^{6}-10^{8}$	changes the magnetic alignment of the nuclei of some atoms	[illegible]

INFRARED SPECTROSCOPY (IR)

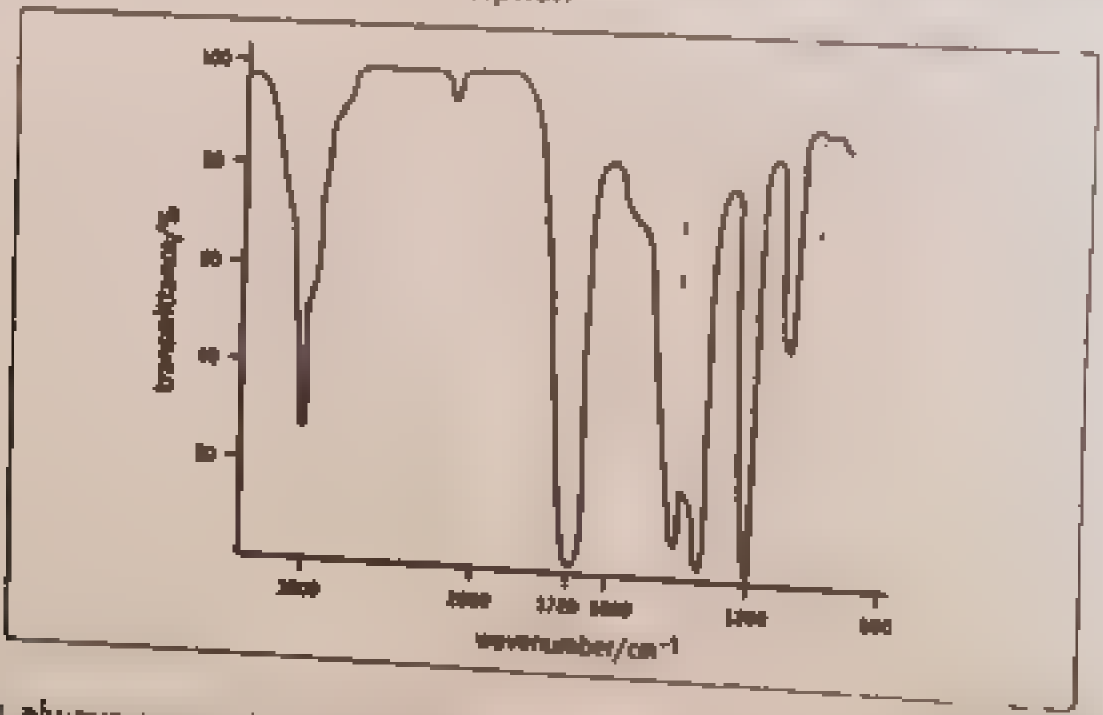
- The molecules absorb infrared (IR) radiation which has a wave ...
- The commonly used IR radiations have range between about ...

Theory and Importance

- The energy of the absorbed IR radiation makes the bonds vibrate as shown in the fig. When the molecule absorbs the radiation the bonds vibrate more energetically.
- Different bonds absorb radiation of different frequencies. The absorbed frequency is the characteristic of a particular bond. Thus IR absorption can be used to identify the bonds, and therefore the functional groups in an organic molecule.
- The figure shows that the effect of IR radiations of vibration of HCl. When an HCl molecule absorbs infrared radiation, it vibrates more energetically. The frequency of radiation absorbed is 7.21x10 Hz and this frequency is characteristic of the H-Cl bond.

Interpretation of IR spectrum:

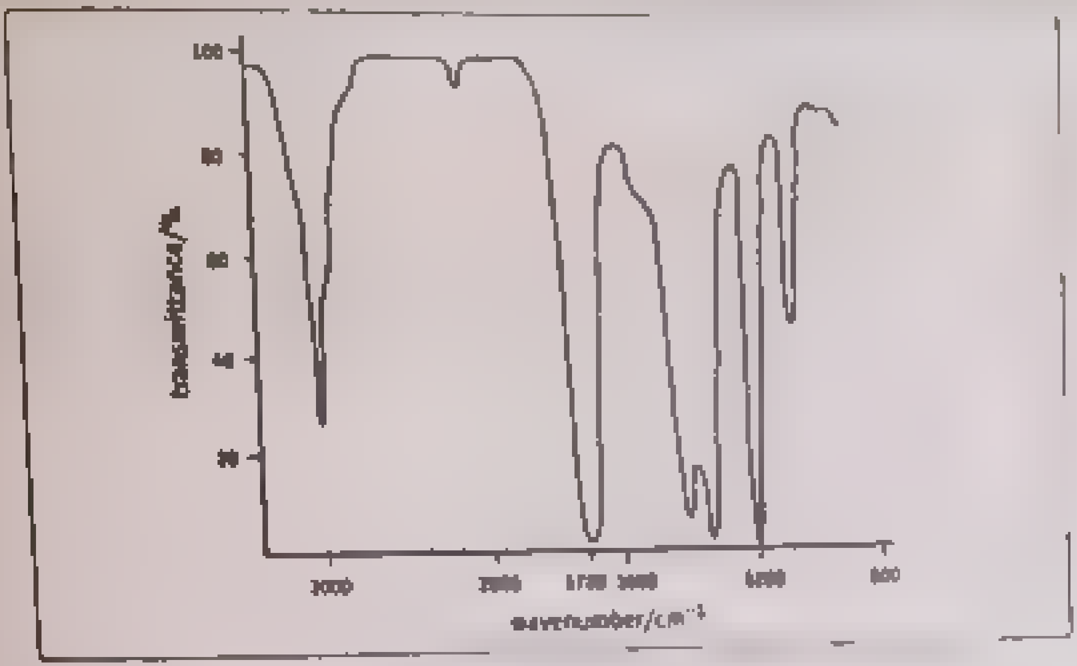
- The IR spectrometer produces an infrared spectrum on a chart recorder as shown ... spectrum contains several peaks of absorption.

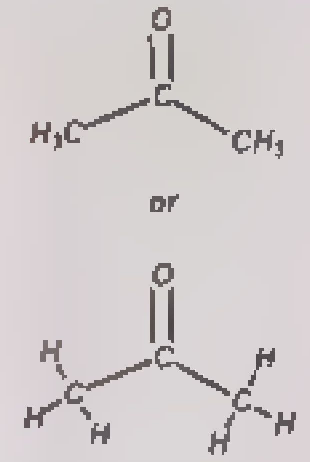


- There are always some characteristic peaks of absorption which can identify func... molecule. The characteristic absorption of some common bonds is given in the table.
- Infrared spectra are very useful, they are particularly helpful for identifying the func... unknown compound.
- In IR spectroscopy the strength of the peak is a characteristic of the bond itself not ... bonds present.
- Most of the interesting parts of an IR spectrum are found in the region above about 1500 ... functional group region.
- The peaks below this region are less useful. It is called fingerprint region. Because it's help... the fingerprint of the compound, the characteristic pattern of its IR spectrum. The fingerpr... to compare the compound's spectrum with IR spectra of known compound given in standard ... books.

Example 1. IR spectrum of Porpanone (Acetone).

The given spectrum is the IR spectrum of propanone (acetone, CH_3COCH_3)



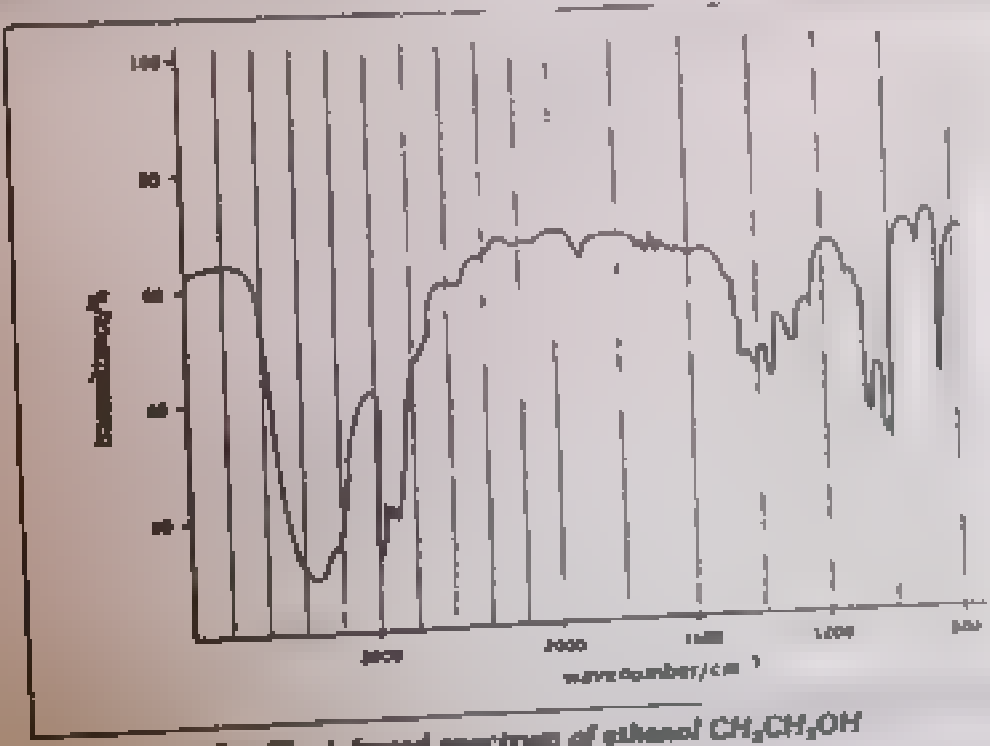


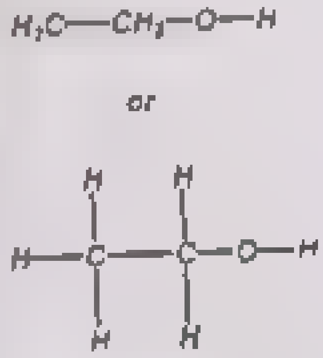
Propanone (Acetone)

Fig. The infrared spectrum of propanone

- The propanone is a simple molecule with only three types of bond. However, the spectrum is quite complicated. It is because each bond can vibrate in different ways and the vibrations can interact with each other.
- The IR spectrum of propanone consists of two characteristic peaks
  - ✓ The strong peak at about $1720cm^{-1}$ corresponds to the C=O bond
  - ✓ The weaker absorption at $3000cm^{-1}$ corresponds to the C-H bond. This peak is weaker even though there are more H atoms in the molecule

Example 2. IR spectrum of Ethanol:





Ethanol

Fig. The infrared spectrum of ethanol CH_3CH_2OH

In the IR spectrum for ethanol following are the characteristic peaks

- The peak just below $3000cm^{-1}$ is from the C-H bonds
- The peak at about $3400cm^{-1}$ is from the O-H bond

QUICK QUIZ-2

Figure 24.5 shows the IR spectrum of ethanol, CH_3CH_2OH ...

(i) **What bond gives rise to the peak just below 3000cm^{-1}?**

This is due to C – H ...

(ii) **What bond gives rise to the peak at about 3400cm^{-1}?**

This is due to O – H stretching vibration. The broad ...

ULTRAVOILET AND VISIBLE SPECTROSCOPY (UV-Vis)

Emission spectrum

When electrons of a substance ... radiations of certain frequencies. It ...

The radiation may be ...

Examples and Theory:

- When sodium chloride is heated ... flame ...
- Consider methylene blue, an ... When white light shines on methylene blue, some electrons in the dye's molecules ... absorb certain frequencies of light and change their energy ... The absorbed radiation ... the red end of the spectrum. If red is removed from white light, the ... becomes blue. The ... can only be noticed ... light is shining on it. This is an example of a visible absorption spectrum, where a chemical ... frequencies of visible radiation.
- Ultraviolet radiation can be absorbed in a similar way; it is not visible but can be detected by instruments. By finding which frequencies have been absorbed, chemists can get information about the ... Consider an aqueous solute of titanium (III) chloride. This contain the octahedral complex ... $[Ti(H_2O)_6]^{3+}$, and $Cl^-(aq)$ ions. A solution of titanium(III) chloride is violet. An absorption spectrum shows that the solution absorbs most effectively in the green-yellow region of the spectrum ... violet radiations are absorbed less efficiently, so the solute looks violet. Both water and Cl^- ... so the Ti^{3+}(aq) ion must be responsible for the color of the solution.

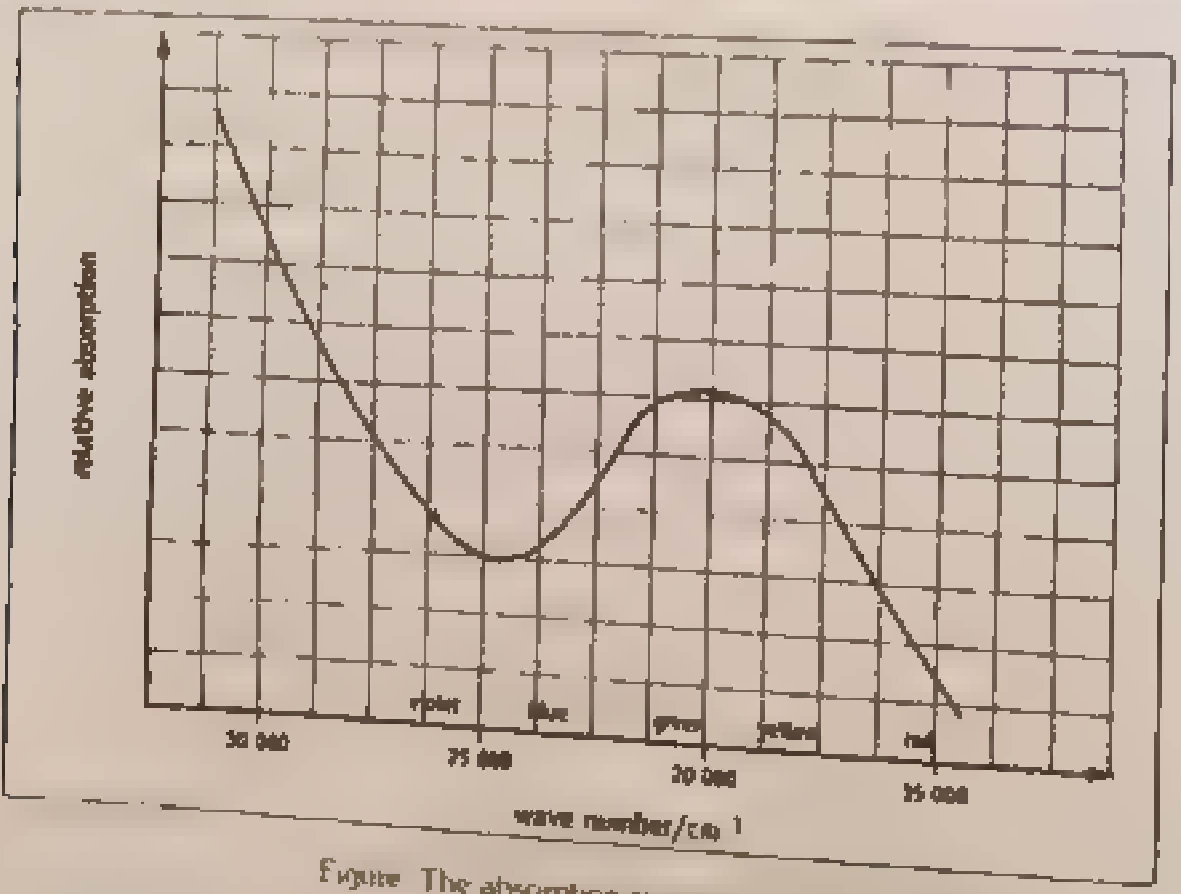


Figure: The absorption spectrum of $[Ti(H_2O)_6]^{3+}$

...ortance.

- By examining the frequencies emitted, chemists can get information about the subst[illegible] It particularly gives information about conjugation and extent of conjugation in a substance.
- The emission spectrum of hydrogen gave chemists the first [illegible] atom.
- Generally, higher the conjugation in a substance, higher will be the [illegible]

...strumentation and Working.

- In an ultraviolet/visible spectroscope, radiation consisting [illegible] passed through a sample of a compound.
- A detector measures the frequencies of absorbed radiations and [illegible]
- The figure shows the ultraviolet/visible absorption spectrum of [illegible] the wavelengths of radiation absorbed in nanometers (nm). The [illegible] i.e., how strongly it is absorbed.
- The ultraviolet/visible spectrum of an organic compound [illegible]
- The compound can be identified by comparing its spectrum with the [illegible]

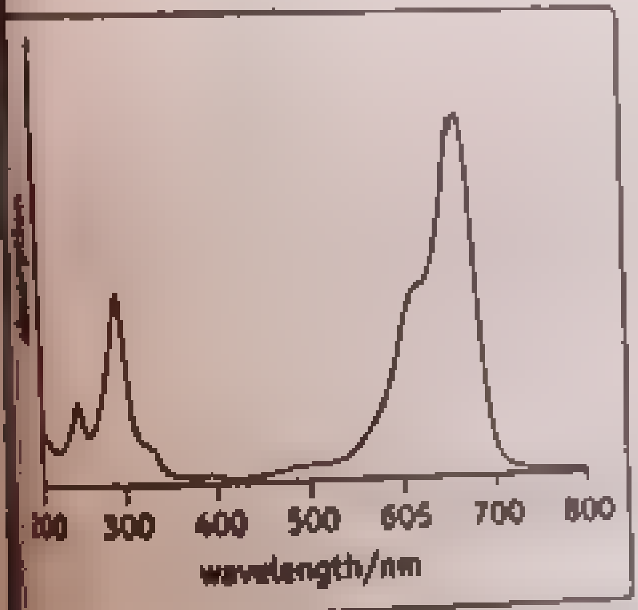


Figure: The visible/UV spectrum of methylene blue

The approximate wavelengths of visible radiation of different colours

Colour	Approximate wavelength/nm
[infrared]	above 700
red	620–700
orange	600–620
yellow	580–600
green	520–580
blue-green	490–520
blue	440–490
indigo	420–440
violet	400–420
[ultraviolet]	below 400

Note:
UV-Vis spectroscopy is an important technique for the detection of compounds. However other types of spectroscopy particularly infrared and nuclear magnetic resonance, are more useful for determining the [illegible] of an organic compound.

NUCLEAR MAGNETIC RESONANCE (NMR)

Theory

- [illegible] they [illegible] possess [illegible]
- The [illegible] nucleus. Hence [illegible] out and [illegible] a magnetic field.
- If the [illegible] just as a compass needle [illegible]

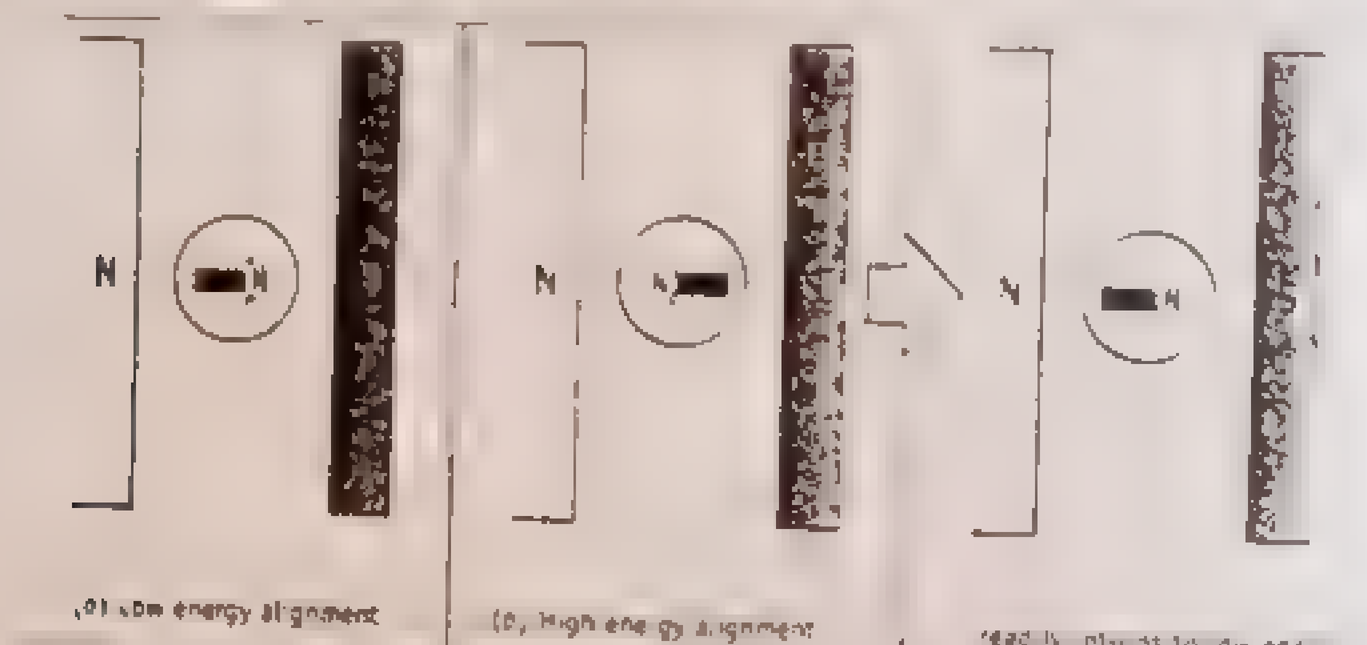


Figure: [illegible]

- The nuclear magnet can have two alignment of low and high energy as shown in the [illegible] magnet can be changed from low energy to the high energy alignment by supplying [illegible] spin flipping

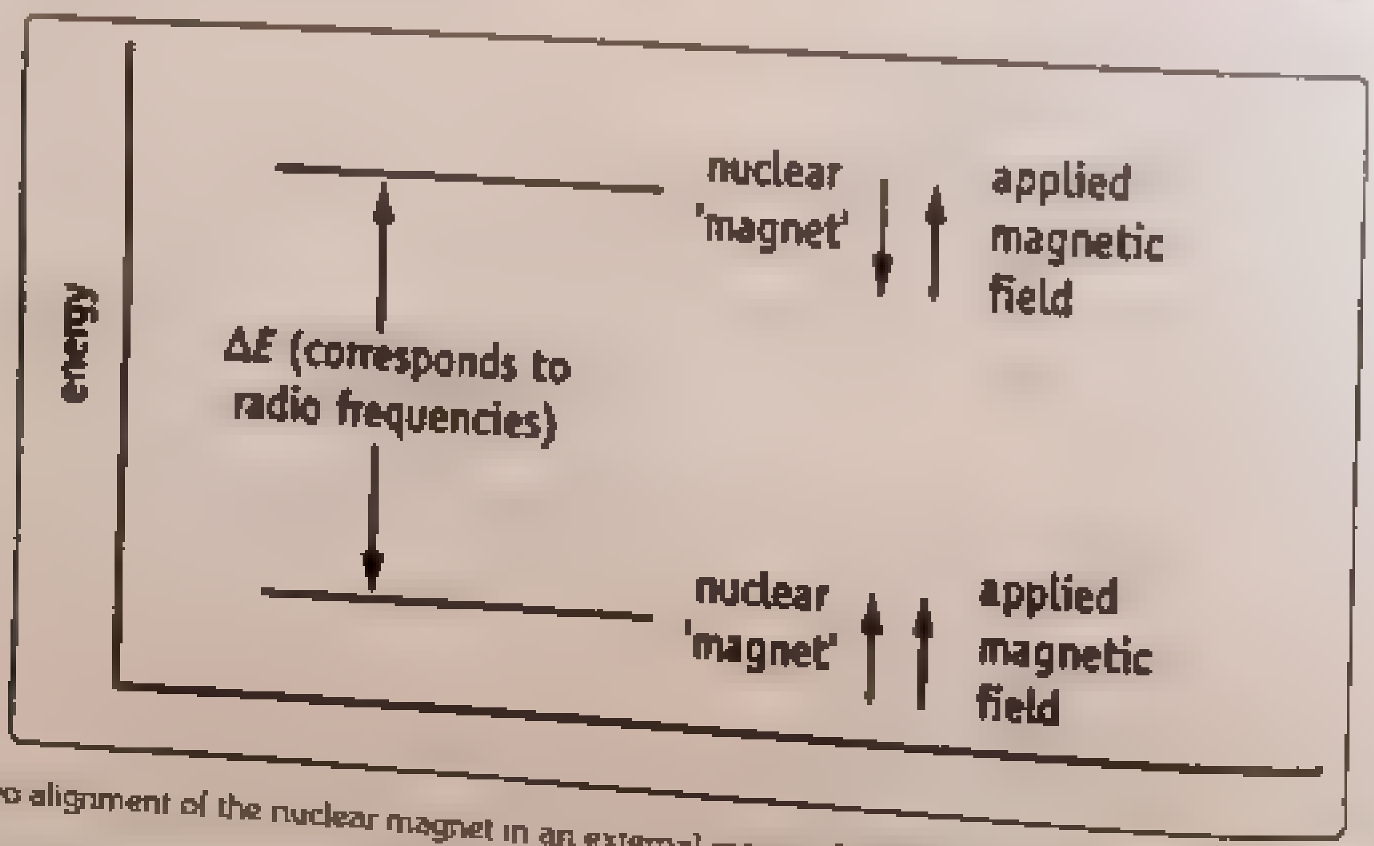


Figure: Two alignment of the nuclear magnet in an external magnet field. The energy difference between [illegible] orientations is the basis of the technique of NMR

- The energy required for spin flipping is provided by radio frequency radiations

- The exact frequency of energy depends on the en[illegible] nuclei and electron in its neighborhood
- Hence, when a sample is placed in a strong magnetic field different [illegible] different frequencies of radiation. This technique is called nuclear magnetic [illegible] spectroscopy
- The result is recorded in the form of an NMR spectrum [illegible] signals [illegible]. In NMR spectrum the chemical shift values are present on X axis and intensity of absorption on Y axis

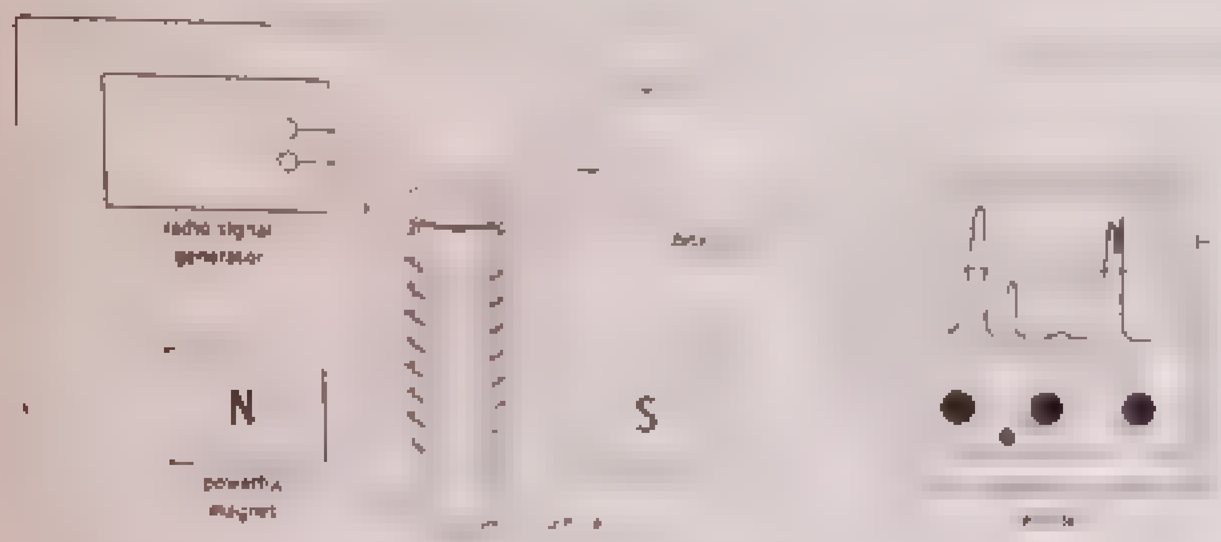


Figure: A simplified NMR spectrometer. The sample is dissolved in a s[illegible] have nuclear magnetic properties

IMPORTANCE OF NMR

- The technique of NMR is particularly useful for identifying the [illegible] type of hydrogen atoms [illegible] H in a molecule
- It is also used to find the position of carbon atoms. The common isotope of carbon [illegible] does not have a nuclear magnet but natural carbons contains 1% of the [illegible]C isotope which does show magnetic behavior and can be identified using NMR.

Exercise Q3 (iv) What is meant by the term chemical shift of a particular proton in NMR spectroscopy? Also draw the splitting pattern of protons in NMR spectrum of ethyl alcohol [illegible]

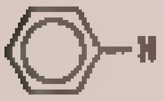
CHEMICAL SHIFT

The separation of a signal in NMR spectrum from a reference point is called chemical shift

It is denoted by δ.

- The H atoms in a particular type of environment have similar positions in the NMR spectrum. [illegible] this position is measured as a chemical shift form a fixed reference point. The reference [illegible] used is the absorption of a substance known as TMS. The chemical shift of TMS is set at zero
- TMS stands for tetramethylsilane, $Si(CH_3)_4$. This non toxic and unreactive substance [illegible] chosen as the NMR reference because its protons give a single peak that is well separated from [illegible] NMR spectra of most organic compounds

The following table gives the chemical shifts for some common proton environments

Type of proton	Chemical shift, δ, in region of
$R—CH_3$	0.9
$R—CH_2—R$	1.3
$R—CH(R)—R$	2.0
$—C(=O)—CH_2—$	2.3
$—O—CH_3$	3.8
$—O—CH_2—R$	4.0
$—O—H$	5.0
	7.5
$—C(H)=O$	9.5
$—C(O—H)=O$	11.0

Intensity of Absorption

In NMR spectrum the intensity of absorption on Y-axis gives the number of nuclei present in a ... environment. The relative ratio of area under each peak is measured by an integrator present ... spectrometer.

INTERPRETATION OF NMR SPECTRUM

Example 1:

- Consider the NMR spectrum of ethylbenzene $C_6H_5CH_2CH_3$ as shown in the figure

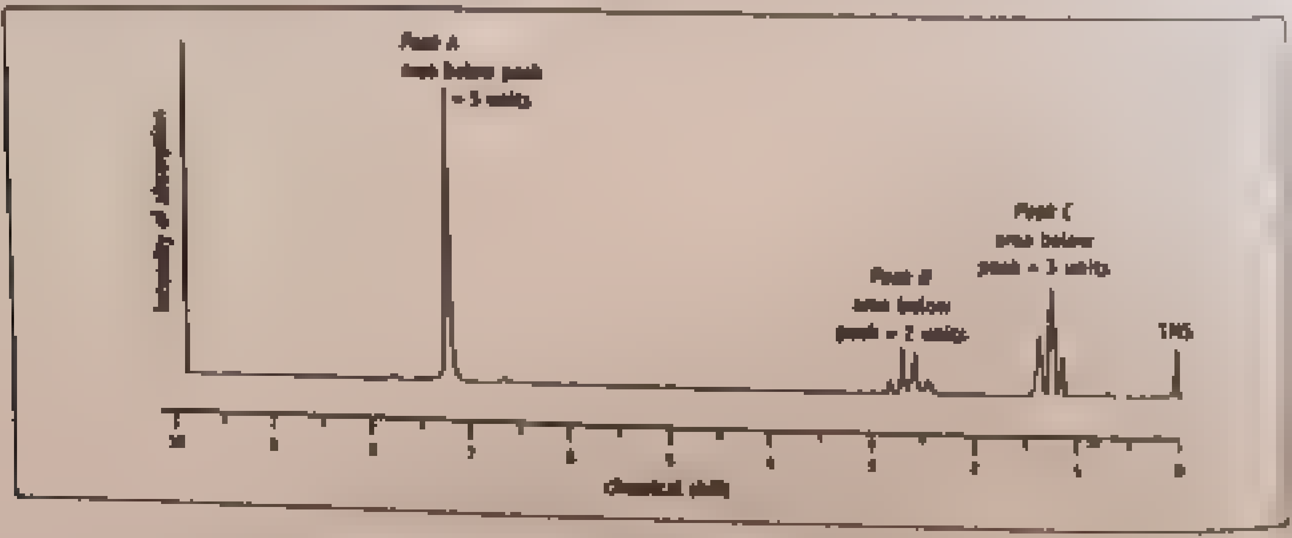


Figure The proton NMR spectrum of ethylbenzine, $C_6H_5CH_2CH_3$

- This is a proton NMR spectrum the frequencies correspond to the absorption of energy by H nu... which are protons. There are three major peaks of differing heights.

- Each peak corresponds to H atoms in a different molecular environment. The area under each peak is proportional to the number of that type of H atom in the molecule
- The largest peak (A) corresponds to the 5 H atoms in C_6H_5, the benzene ring
- The second largest (C) corresponds to the 3 H atoms in the $-CH_3$ group
- The third peak (B) corresponds to the 2 H atoms in the CH_2 group

Example 2-

- The following figure shows a simplified proton NMR spectrum for ethanol CH_3CH_2OH
- It has been simplified by removing some of the detail, so the peaks appear single
- The peak for TMS is also present
- The integrated trace is also shown which gives the relative areas under each of the peaks

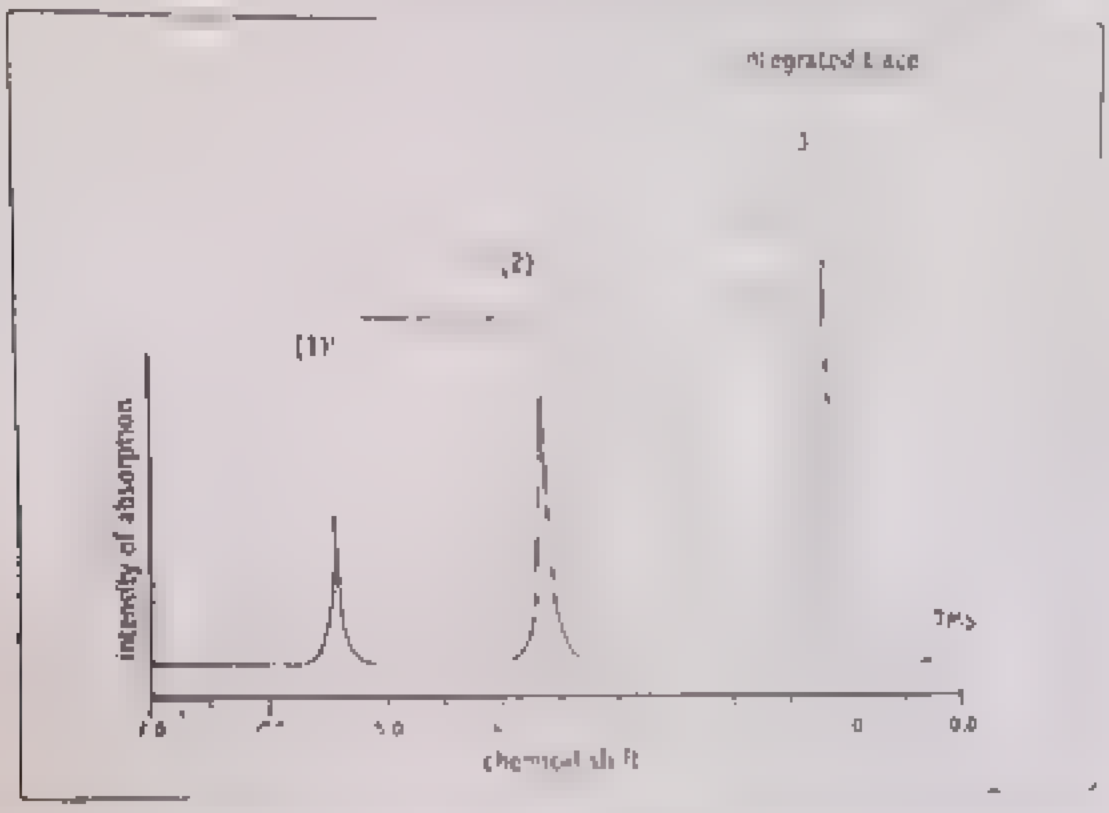


Figure A simplified proton NMR spectrum for ethanol CH_3CH_2OH. The integrated trace shows that areas under the peaks are in the ratio 1:2:3

From the table of chemical shift values, the spectrum of ethanol can be interpreted as

- The largest peak (3) corresponds to the 3 H atoms in $-CH_3$
- The second largest peak (2) corresponds to the 2 H atoms in the $-CH_2$ group
- The third peak (1) corresponds to the 1 H atoms in the $-OH$ group

QUICK QUIZ-3

(i) ***Use table to identify each of the peaks in figure (NMR spectrum of ethanol***

Approximate chemical shift values (δ values)	***Nature of proton***
About 5.4	Hydroxyl protons –OH
About 3.5	Methylene protons –CH_2
About 1.3	Methyl protons –CH_3

(ii) Explain the relative areas under the peaks

The ratio of relative height of integrated trace in the NMR spectrum is

Peak (1) : **Peak (2)** : **Peak (3)**

1 : 2 : 3

Thus

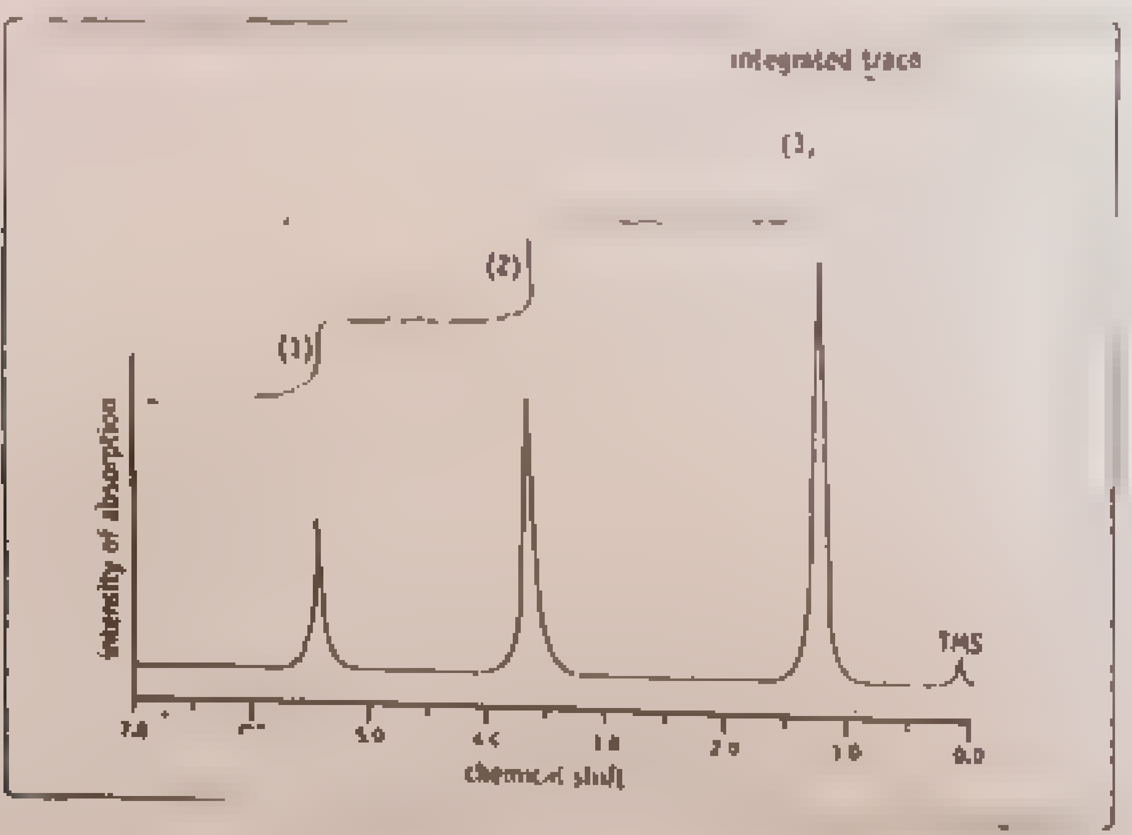
- Peak (1) corresponds to one proton (due to OH)
- Peak (2) corresponds to two protons (due to CH_2)
- Peak (3) corresponds to three protons (due to CH_3)

SPIN-SPIN COUPLING:

In NMR the magnetic interaction of neighboring nuclei with each other is called spin-spin coupling

In NMR the splitting of signal of a particular nucleus due to spin spin coupling with neighboring nuclei is called spin-spin splitting.

Consider the simplified NMR spectrum of ethanol as shown below



It shows three single peaks.

- The smallest peak corresponds to the single OH proton
- The middle peak corresponds to the two CH_2 protons
- The largest peak corresponds to the three CH_3 protons.

A detailed high-resolution spectrum of ethanol shows that the CH_2 and CH_3 peaks are in fact split into a number of subsidiary peaks as shown in the figure below. This splitting is caused by spin spin coupling between protons on neighboring carbon atoms.

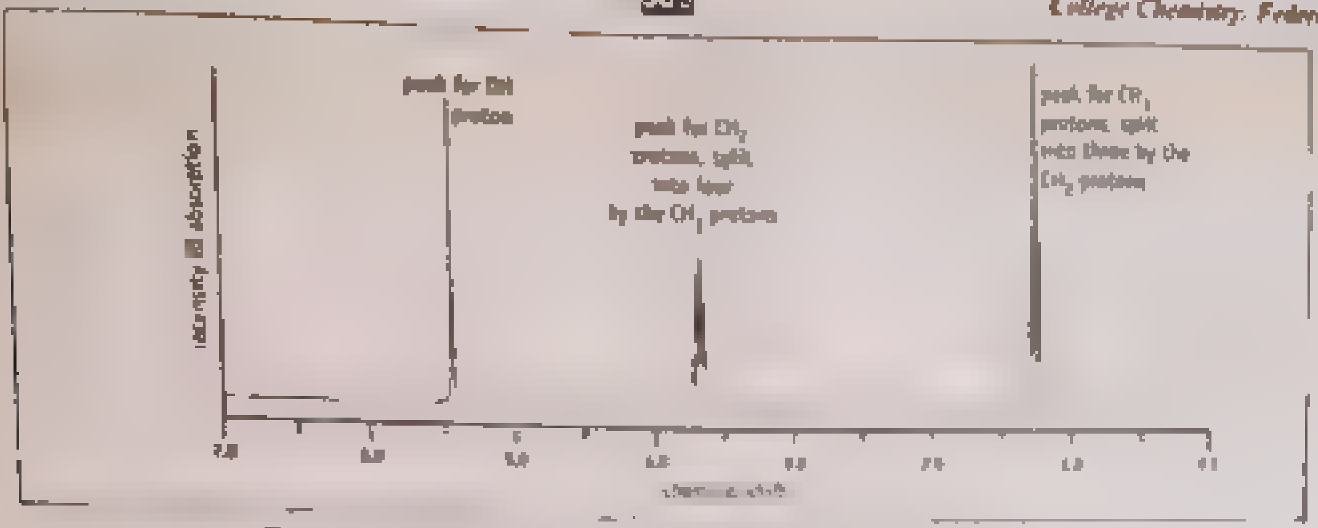


Figure: A detailed high resolution NMR spectrum for ethanol

Explanation of spin-spin coupling

- One of the carbon atoms in ethanol has two protons on it (CH_2). The other has three protons on it (CH_3). Consider CH_3 protons which [illegible] applied, these three tiny magnets can arrange themselves in four different ways

  (i) All three aligned with the magnetic field
  (ii) All three aligned against the magnetic field
  (iii) Two aligned with the field and one aligned against it
  (iv) On aligned with the field and two aligned against it

Each of these four arrangements gives a slightly different overall [illegible]. So each different field interacts with the neighboring CH_2 protons slightly differently.
Thus, these CH_2 protons give four different peaks very close to one [illegible] peaks are called **a quartet**

- Similarly the two protons on the CH_2 group can arrange themselves differently [illegible] external magnetic field. This time there are three different arrangements

  (i) All two aligned with the magnetic field
  (ii) All two aligned against the magnetic field
  (iii) One aligned with the field and one aligned against it

Each of these different fields interacts with the neighbouring CH_3 protons [illegible]. Thus, these CH_3 protons give three different peaks very close to [illegible]. These three peaks are called **triplet**.

General rule:
A group carrying "n" protons will cause the protons on a neighbo[illegible] split into 'n + 1' peaks

Hence, a high-resolution spectrum can be interpreted as

- Use the position of each overall peak to identify the type of protons causing the peak
- Use the integrated trace to find the number of each type of proton
- Use the n + 1 rule above to get information about the number of protons o[illegible]

QUICK QUIZ-4

(1) Which type of nucleus has magnetic filed

If a nucleus has an even ... overall magnetic field ...

(2) What happens when a magnetic nucleus is placed in magnetic filed

If a magnetic n... placed in an external magnetic field the nuclear m... nuclear magnet can have two alignments

- One is of low energy, which is along the external magnet field and
- Other is of high energy which is against the external magnetic field

(3) What is nuclear magnetic resonance spectroscopy

It is an analytical technique used to find the nature of nuclei having magnetic moment (e.g. protons) in presence of external magnetic field

The nuclei which have magnetic moment can take up two orientations in external magnetic field of low energy and the other of high energy. The low energy state can be converted into high ... by supplying ... frequency region. The exact frequency of energy depends ... environment ... protons in a molecule absorb different frequencies ... and thus they can be ...

(4) What information is obtained from NMR spectrum

In NMR spectrum ... peaks are present. These peaks give two information

- The position ... on X axis gives the nature of nuclei present in a particular environment
- The intensity of absorption on Y axis gives the number of nuclei present in a particular environment

(5) What information are obtained from numbers of peaks and area under peaks in NMR spectrum

- The number of peaks gives the types of nuclei in different environment
- The area under peaks gives the number of nuclei in a particular environment

(6) What is NMR reference?

In NMR spectrum the position of a particular peak is measured as a chemical shift form a fixed reference point. The reference point normally used is the absorption of a substance known as Tetramethyl... TMS. The chemicals shift of TMS reference is set at zero

(7) Why splitting of peaks occur

In NMR, the splitting of signal of a particular nucleus due to spin spin coupling with neighboring ... called spin spin splitting

Let there is a particular nucleus having magnetic moment in a molecule. The magnetic nuclei ... atoms may have different magnetic field due to their different alignments. So, each neighboring different ... interacts with a particular nucleus slightly differently. Thus, the signal of a particular nucleus is split up

Exercise Q3 (a) What is the basic principle of Atomic Absorption Spectroscopy? Describe ... instrumentation used

ATOMIC EMISSION SPECTROSCOPY (AES)

In atomic emission spectroscopy electronic transitions occurs in atoms. It is done by an excitation ... flames sparks. It ... shows the characteristic radiation produced when atoms are ex... atoms emit radiat... lower energy states ... wavelengths of light called spectral lines which ...

Principle

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy E_2 undergoes a transition to a state of lower energy E_1 and a photon of energy $h\nu$ is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies

Advantages of Emission Spectroscopy

Emission method is extremely important in analysis

(1) This technique is highly specific

(2) This method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration.

(3) Even metalloids have been identified by this technique

(4) This analysis can be performed either in solid or liquid state with almost equal convenience

(5) This technique requires minimum sample preparation as a sample can be directly introduced into the spark

(6) The technique provides results very rapidly. If automated, time required is just 30 sec to one minute

(7) This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, environmental and biological samples

Disadvantages of Emission Spectroscopy

(1) The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.

(2) Recording is done on a photographic plate which takes some time to develop, print and interpret the results

(3) Radiation intensities are not always be reproducible.

(4) Relative error exceeds 1 to 2 %

(5) The accuracy and precision are not high

Applications:

(1) Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes

(2) Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analyzed.

(3) Lubricants oils have been analyzed for Ni, Fe, Cr, Mn, Si, Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and tear need of engine overhaul

(4) In petroleum industry oil is analyzed for V, Ni, Fe the presence of which makes fuel poor

(5) Solid samples and animal tissues have been analyzed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc

(6) Emission spectroscopy has been used to detect 40 elements in plants and soil. Thus metal deficien[illegible] and oil can be diagnosed

(7) The following materials have been analysed by emission spectroscopy

(i) Trace and major constituents in ceramics

(ii) Traces of Co, Ni, Mo and V in Graphite

(iii) Trace metal impurities in analytical regents

(iv) Trace of Ca, Cu, Zn in blood

(v) Zinc in pancreatic tissues

QUICK QUIZ-5

3. ... [illegible] ... by emission spectroscopy

4. ... [illegible] ... metallurgy

ATOMIC ABSORPTION SPECTROSCOPY (AAS)

Quick Quiz-6. 1. Give principle of atomic absorption spectroscopy

Principle of AAS

Quick Quiz-6. 2. Give few application of atomic absorption spectroscopy

Applications of Atomic Absorption Spectroscopy (AAS)

1. The AAS technique has become the most powerful tool of ...
2. [illegible]
3. [illegible]
4. [illegible]

QUICK QUIZ-6

1. Give principle of atomic absorption spectroscopy

See p. 512

2. Give few application of atomic absorption spectroscopy

See p. 512

Exercise Q3 (vii) What is the basic principle of Mass Spectrometer? How does it work?

MASS SPECTROMETRY (MS)

The mass spectrometer is an instrument which turns atoms and molecules into ions ...

- In 1919 Aston invented the mass spectrometer. This gave chemists a reliable and accurate method of comparing the relative masses of atoms.
- At one time, the relative masses of atoms were known as atomic weights but now we refer to them as relative atoms masses.

Basic Principle:

The basic idea of a mass spectrometer can be demonstrated using the apparatus ... in figure. Wooden balls of different sizes but with identical iron cores, roll down a s... powerful magnet attracts the iron cores and the moving balls are defle...

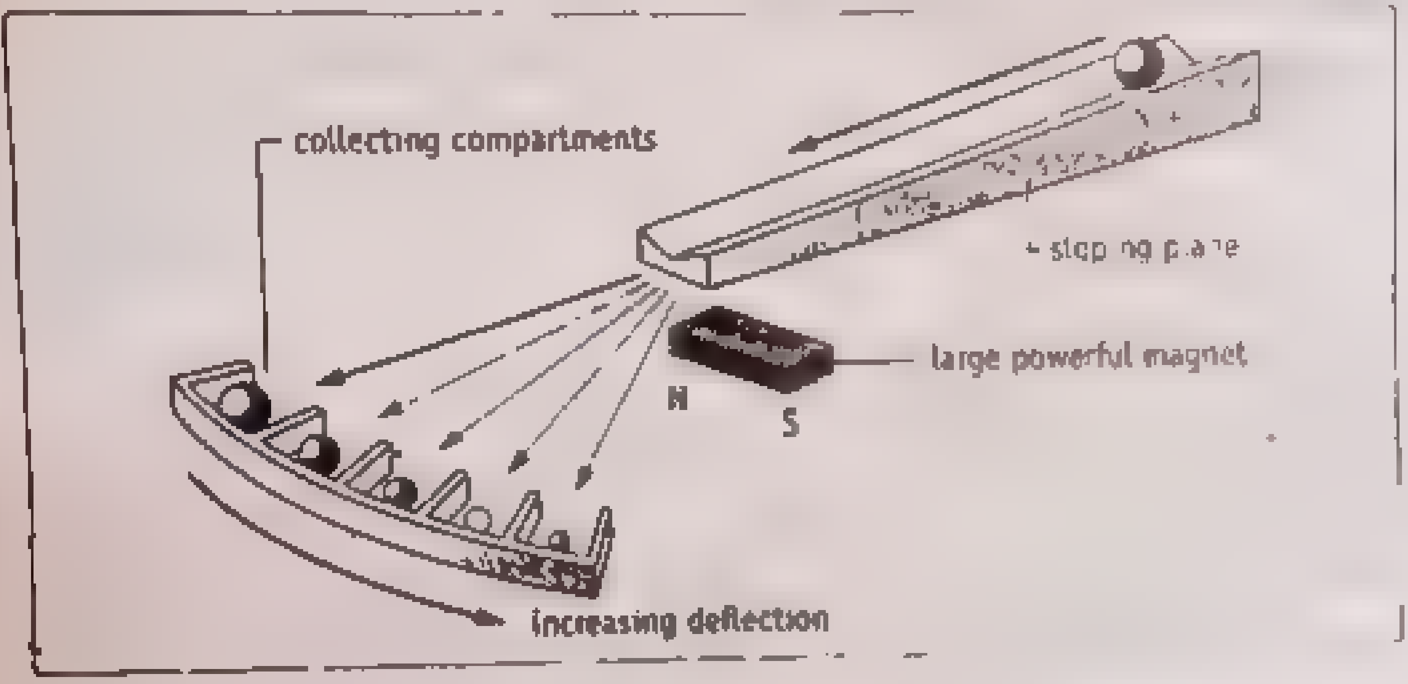


Figure: A simple model to illustrate the working of a mass sp...

- As the balls have identical iron cores, they are all attracted equally ... lighter, therefore they are deflected the most. The balls collect in ... mass. All balls of the same mass collect in the same compartment. Using this simple apparatus, it is possible to separate the different sized balls according to their mass and to find the ...
- A real mass spectrometer works in a similar fashion to this simple ... their mass and shows the relative numbers of the different atoms ... and separated, they must be converted to positively charged ions.

QUICK QUIZ-7

(1) Why does the magnet have the same attraction for all the balls?

Since the balls have identical iron cores, they ...

(2) Which size of ball will be deflected the most? Why?

The smaller balls are lighter, therefore ...

Mass Spectrometer Working

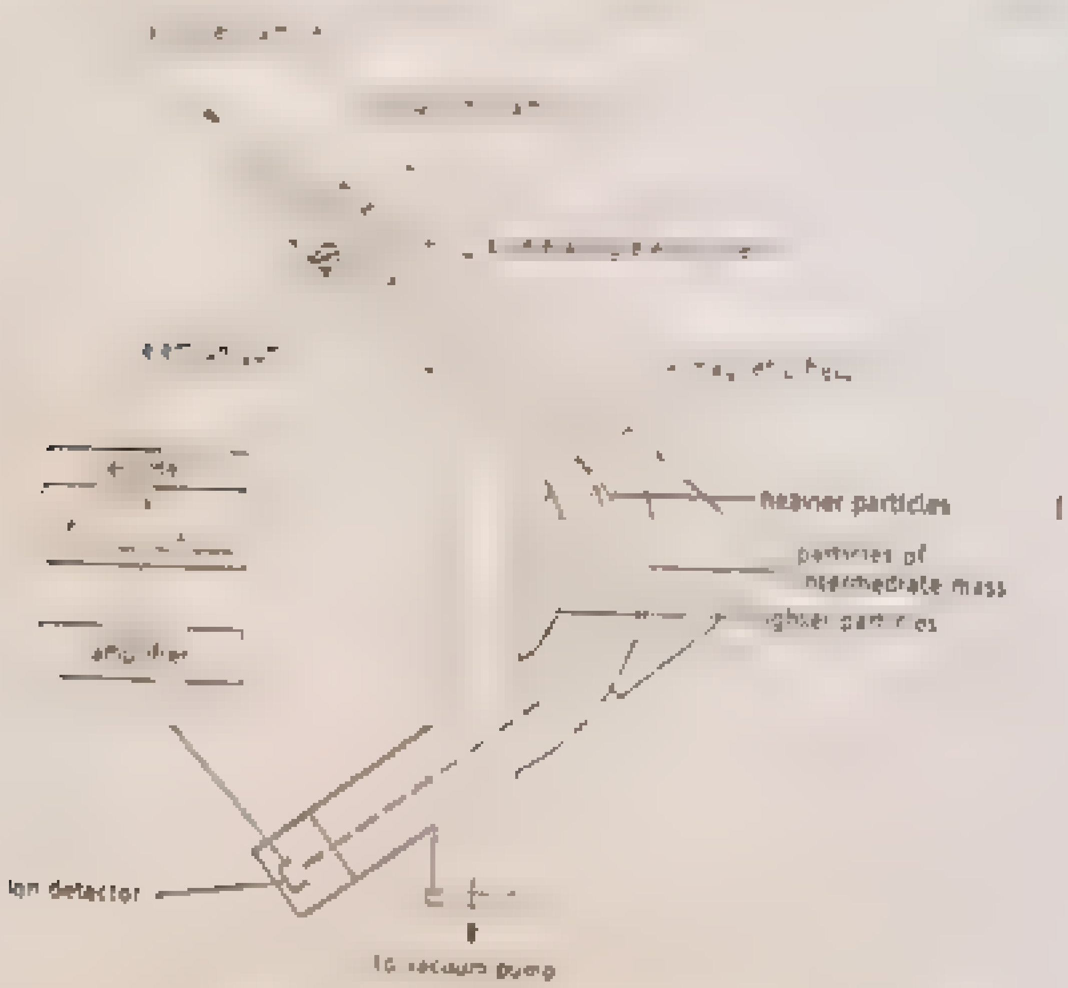


Figure A diagram of a mass spectrometer

Instrumentation and Working

It can be explained as follows

1 – Vaporization

- Gases, liquids and volatile solids are injected into the instrument just before the ionization chambe
- Less volatile solids must be preheated to vaporize them

2 – Ionization

- After vaporization the elements passes into the ionization chamber
- Here atoms of the elements are bombarded with a stream of high energy electron
- This causes ionization. One or occasionally two electron are knocked out of the atoms leaving ions

Example

e^-	+	X	$\rightarrow$	X^+	+	e^-	+	e
high-energy electron		atom		positive ion		electron knocked out of X		high energy electron retreating

or occasionally

$$e + X \rightarrow X^{2+} + \underbrace{e^- + e^-}_{\text{2 electrons knocked out of X}} + e$$

3 – Acceleration

- These positive ions such X^+ and X^{2+} now pass through holes in parallel [illegible]
- An electric field is applied to accelerates the ions into the instrument towards [illegible]

4 – Deflection

- As the ions pass through the magnetic field they are deflected according to [illegible] charge
- The particles can only pass through the instrument if they are [illegible]

5 – Detection

- If the accelerating electric field and the deflecting magnetic field are [illegible] ions of only one particular mass/charge ratio will hit the ion detector at the end of the [illegible]
  - ✓ Ions of smaller mass/charge ratio will be deflected too much
  - ✓ Ions of greater mass/charge ratio will be deflected too little
- The ion detector is usually linked through an amplifier to a recorder
- As the strength of the magnetic field is slowly increased ions of [illegible] mass will be detected and mass spectrum is traced out by the recorder as shown in the figure

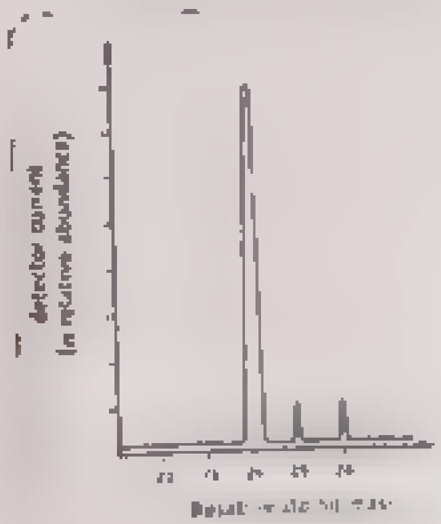


Figure- A mass spectrometer trace for naturally occurring [illegible]

- The relative heights of the peaks in the mass spectrum give a [illegible] ions present
- In practice a reference peak using a known substance is first obtained on the [illegible] masses of other particles can then be obtained by comparison with this

QUICK QUIZ-B

Look closely at figure 24.15

(1) *How many different ions are detected in the mass spectrum of naturally occurring magnesium?*

Since there are three peaks in the mass spec...

(2) *What are the relative masses of these different ions?*

The position of peaks shows that the relative masses are 24, 25 and 26.

(3) *What are the relative proportions of these different ions?*

The ions with relative mass 24 is most abundant ... comparatively less abundance. However, both these have ...

SOCIETY, TECHNOLOGY AND SCIENCE

FORENSIC CHEMISTRY

Forensic chemistry is the application of chemistry to criminal investigation

- It deals with criminal investigation in the laboratory analysis of ... evidence.
- It also develops the analytical skills required for other areas of ... such as ... accident investigation and product liability.
- Analytical measurements are essential to everyday life, required to determine ... control the quality of many products, to protect the environment and to ...
- Thus, analytical Chemistry is important not only in chemistry, but also in fields ... and the forensic, food, environmental and pharmaceutical sciences.
- Forensic chemistry is the application of analytical chemistry to the law and ... physical traces such as body fluids, bones, fibres and drugs.
- The success in analytical chemistry requires the ability to make rigorous ... of the principles and practice of modern instrumentation, and a problem solving approach.

Abilities of a Forensic Chemist

- The forensic chemist requires a strong background in chemical analysis and ... must be able to effectively communicate the results of laboratory analysis in ... courtroom.
- The forensic chemist must have a strong theoretical and experimental background ... as well as in problem solving skills.
- Forensic chemists must have good attention to detail and superior problem-solving skills.
- They need critical thinking abilities to solve crime puzzles based on fragmentary evidence.
- Forensic chemists must take accurate notes and make accurate records of their findings. T... strong writing skills to produce clear reports on highly technical subjects so that others can ...

CHEMICAL INSTRUMENTATION AND TECHNOLOGY

- Chemical instruments are used extensively in research and development activities, laboratories ... of the major users.
- Use of chemical instruments for disease diagnosis is on a rise.
- Chemical equipment market is growing at a rapid rate due to the continuous requ... instruments in pharmaceutical and biotechnology industries.
- Besides, the increase in number of biotechnology firms worldwide, advances in life science ... technology innovations with human genome mapping, and emergence of proteomics ... industry growth, as such high end research projects require quality instruments ... capacity. All these factors are driving the life science and chemical instrumentation market.
- The global life science and chemical instrumentation market was estimated to be \$30.2 billion in the year 2011 and is expected to grow at a CAGR of 8.4 % from 2011 to 2016 to reach \$45.2 billion.

CONNECTION BETWEEN CHROMATOGRAPHY AND MS

Chromatography

It is the collective term for a set of laboratory techniques for the separation of mixtures ... for the determination of small amounts of materials present in those mixtures

Principle

- The mixture is dissolved in a fluid called the mobile phase, which carries it through a structure holding another material called the *stationary phase*
- The various constituents of the mixture travel at different speeds, causing them to separate
- The separation is based on differential partitioning between the mobile and stationary phases ... differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation

Mass spectrometry

- It is an analytical technique that measures the mass to charge ratio of charged particles
- It is used
  - ✓ for determining masses of particles,
  - ✓ for determining the elemental composition of a sample or molecule, and
  - ✓ for determining the chemical structures of molecules, such as peptides and other chemical compounds
- It works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios

Gas chromatography–mass spectrometry (GC-MS)

It is a method that combines the features of gas liquid chromatography and mass spectrometry to identify different substances, even present in small amounts, within a test sample

Applications

- These include drug detection, fire investigation, environmental analysis, explosives investigation ... identification of unknown samples.
- GC MS can also be used in airport security to detect substances in luggage or on human beings
- It can identify trace elements in materials that were previously thought to have disintegrated beyond identification
- GC-MS has been widely heralded as a "gold standard" for forensic substance identification ... used to perform a *specific test*. A specific test positively identifies the ... substance in a given sample

Liquid chromatography–mass spectrometry (LC-MS) or alternatively, HPLC MS

It is a chemistry technique that combines the physical separation capabilities ... chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry

It has very high sensitivity and selectivity

Applications

- Generally its application is oriented towards the ... chemicals in the presence of other chemicals ...
- Preparative LC-MS system can be used for fast and ... extracts and new molecular entities important to food, p... industries

Limitations

- The limitations of LC-MS in urine analysis drug screening is that it often fails to d... specific metabolites, in particular with hydrocodone ...

KEY POINTS

- [illegible]
- The molecular [illegible] the empirical formula once th[illegible]
- [illegible] arrangement of atoms. It can be found from a know[illegible] NMR
- The instrument that is used to measure the amount of electromag[illegible]
- Absorption of infrared radiation causes covalent bonds within the molecule to be promoted from vibrational energy level to a higher [illegible]
- Stronger bonds [illegible] greater energy to vibrate. Therefore such bonds absorb infrared radiation [illegible]
- Different functional [illegible] radiation at different wavelengths and their presence absence in a molecule can be de[illegible] by examination of an IR spectrum
- No two compounds have ex[illegible] red spectra
- Absorption of ultraviolet [illegible] causes electrons within molecules to be promoted from energy level to a higher electronic energy level
- [illegible] absorb UV-Vis radiation [illegible] that the compound does not con[illegible] conjugated double bonds
- If an organic compound absorbs UV-Vis radiation it [illegible] the compound contains a carbon[illegible] conjugated double bonds. For example [illegible] compounds all absorb in the UV-Vis region
- Absorption of radio waves in the presence of a magnetic field causes nuclei within molecules [illegible] promoted from one spin energy level to a higher spin energy level
- The number of signals in the NMR spectrum corresponds to the number of different types of protons [illegible] molecules
- The position (chemical shift) of each signal gives information about the structural environment [illegible] protons
- The relative areas (integration) under the signals give the ration of the numbers of each type of pro[illegible] in the molecule. If the molecular formula is known, the actual number of each type of protons ca[illegible] determined
- The splitting pattern of each signal gives us the number of protons on neighboring carbons. The numb[illegible] of peaks into which a signal is split a signal is split is one more than the total number [illegible] directly adjacent carbons
- Emission spectroscopy is concerned with the characteristic radiation produced when atoms are [illegible] They emit radiations in the form of discrete wavelengths of light called spectral lines whe[illegible] the lower energy states
- Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usuall[illegible] neutral atoms in the gaseous states. If light of the resonance wavelength passes through a [illegible] containing the atoms, then part of the light will be absorbed, and the extent of absorptio[illegible] proportional to the number of ground state atoms present in the flame
- Mass spectroscopy involves organic molecules being bombarded by a very high energy electron bea[illegible]
- The peak of highest intensity in a mass spectrum is referred to as the base peak
- Fragmentation processes can produce numerous fragments from which the structures [illegible] molecules can be deduced
- When one electron is removed from a molecule, a molecular ion is produced. The m/e value [illegible] molecular ion peak is the molecular weight of the compound being investigated. The molecular [illegible] obtained by mass spectroscopy are extremely accurate

EXERCISE

Q1: Select the right answer from the choices given with each question.

Which of the following techniques does not involve electromagnetic radiations?
(a) Infrared spectroscopy (b) NMR spectroscopy
(c) Mass spectroscopy (d) All of these involve electromagnetic radiations

Which region of the electromagnetic spectrum is involved in the electronic excitations?
(a) Ultraviolet (b) Visible
(c) Both of these (d) None of these

Which of the following techniques is different from the others as regards the basic principle?
(a) Ultraviolet spectroscopy (b) [illegible]
(c) Electronic spectroscopy (d) None of these

Which of the following is used as a source of visible radiations?
(a) Tungsten filament lamp (b) Hydrogen discharge lamp
(c) Deuterium discharge lamp (d) All of these

What is the wavelength range of the ordinary infrared region?
(a) 0.8-2.5 μm (b) 2.5-16 μm
(c) 16-1000 μm (d) 400-800 nm

(vi) *The position of an infrared absorption band is commonly expressed by*
(a) Wavelength (b) Wave number
(c) Both of these (d) None of these

(vii) *Which of the following is not used as a source of infrared radiations?*
(a) Nernst filament (b) Tungsten filament
(c) Globar (d) None of these

(viii) *Which region of the electromagnetic spectrum is involved in mass spectrometry?*
(a) Visible (b) Microwave
(c) Radiowave (d) None of these

(ix) *Mass spectroscopy is an analytical technique which involves*
(a) Production of gaseous ions form the sample
(b) Separation of the gaseous ions
(c) Measurement of the relative abundance of the gaseous ions
(d) All of these

(x) *Mass spectrometry can be used to determine*
(a) Molecular weight (b) Molecular formula
(c) Molecular structure (d) All of these

(xi) *Which of the following species is detected in the mass spectrometer?*
(a) Positively charged species (b) Radicals
(c) Neutral molecules (d) All of these

(xii) *Which of the following species is produced in the ionization chamber of a mass spectrometer?*
(a) Positively charges species (b) Radicals
(c) Neutral molecules (d) All of these

(xiii) *Which kind of information about a positively charged species obtained from a mass spectrum?*
(a) Molecular weight (b) Relative abundance
(c) Both of these (d) None of these

(xiv) *What kind of sample can be studied in a mass spectrometer?*
(a) A gas (b) A liquid
(c) A solid (d) All of these

(xv) *Near ultraviolet region of these electromagnetic spectrum generally lies between*
(a) 10-200 nm (b) 200 to 400 nm
(c) 400-750 nm (d) 300-500 nm

(xvi) *Far ultraviolet or vacuum ultraviolet region generally lies between.*

(xvii) For infrared region of the electromagnetic radiation generally ...

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) Mass spectroscopy

(ii) Ans: (c) Both of these

(iii) Ans: (d) None of these

(iv) Ans: (a) Tungsten filament lamp

(v) Ans: (b) 2.5-16 μm

(vi) Ans: (b) Wave number

(vii) Ans: (b) Tungsten filament

(viii) Ans: (d) None of these

(ix) Ans: (d) All of these

(x) Ans: (d) All of these

(xi) Ans: (a) Positively charged species

(xii) Ans: (a) Positively charged species

(xiii) Ans: (c) Both of these

(xiv) Ans: (d) All of these

(xv) Ans: (b) 200-400 nm

(xvi) Ans: (a) 10-200 nm

(xvii) Ans: (c) 50-1000 μm

Q2: Give brief answers for the following questions.

(i) **What is spectroscopy? Underline its principle.**

Spectroscopy. Spectroscopy involved using instruments to examine the ... chemicals giving information about their molecular structure.

Principle: When electromagnetic radiation, such as light or infrared shines on a ... interact with the radiation in some way. The way a particular chemical interacts ... its molecules and structure.

(ii) **What is meant by wavelength and frequency?**

Wavelength

It is the distance between two adjacent crests or troughs in a beam of radiation

It is denote by λ

Its units are picometer, nanometer or angstrom etc

$$1\ \text{Å} = 10^{-10}\ \text{m},\ 1\ \text{nm} = 10^{-9}\ \text{m},\ 1\ \text{pm} = 10^{-12}\ \text{m}$$

Frequency

It is the number of waves, which passes through a given point in one second.

It is denoted by ν. Its units are cycles s^{-1} or s^{-1} or Hertz (Hz)

$1\ \text{Hz} = 1\ \text{cycles}\ s^{-1}$

(i) ***What is spectrometer? Briefly discuss its working.***

Spectrometer: The instrument used to measure the amount of [illegible] substance is called spectrometer.

Working: In a spectrometer the [illegible] radiations absorbed by a sample are [illegible] spectrum can be used to find information about [illegible]

(ii) ***How will you distinguish between***

(i) 1,3-Pentadiene and 1,4-Pentadiene

1,3-Pentadiene is a conjugated system [illegible] conjugated system [illegible] absorb at higher wavelength and have higher [illegible]

(ii) Benzene and anthracene by UV spectroscopy?

Anthracene molecule has three benzene [illegible] anthracene will absorb at higher wavelength [illegible]

(iii) ***Two isomeric dienes (X) and (Y), having the molecular formula C H, absorb at λ_{max} 223nm and λ_{max} 178nm respectively. Write the structures of the two isomers.***

These are 1,3-Pentadiene and 1,4-Pentadiene.

1,3-Pentadiene is a conjugated system [illegible] conjugated system CH_2 CH CH CH [illegible] (λ_{max}=223nm) than that of 1,4-pentadiene (λ_{max}=178nm)

(iv) ***Give significant application of Atomic Absorption Spectroscopy (AAS)***

(1) This method is well [illegible]

(2) This method is highly [illegible]

(3) The technique is firmly established in analytical chemistry of metallurgy, water supplies and soil analysis.

(v) ***How will you distinguish between 2-Pentanone and 3-Pentanone by using mass spectra?***

2-Pentanone: Its major peak base peak [illegible] 43

3-Pentanone: Its major peak [illegible] 57

Q3: Give detailed answers for the following questions.

(i) ***What is combustion analysis? Describe its different steps.***

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(ii) ***An organic compound consists of carbon, hydrogen and oxygen [illegible] was subjected to combustion analysis 0.5439g of the compound gave 1.039g of CO [illegible] formula of the compounds.***

Solution:

Mass of organic compound

Mass of CO_2

Mass of H_2O

Thus Percentage of C

Percentage of H

Percentage

Percentage of H $= \frac{0.6369}{0.5439} \times \frac{2.016}{18} \times 100 = 13.12\%$

Percentage of O $= 100 - (52.11 + 13.11) = 34.78\%$

Element	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	52.10	$\frac{52.10}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	C_2H_6O
H	13.12	$\frac{13.12}{1.008} = 13.02$	$\frac{13.02}{2.17} = 6$	
O	34.78	$\frac{34.78}{16} = 2.17$	$\frac{2.17}{2.17} = 1$	

Thus the empirical formula for the organic compound is C_2H_6O

(iii) ***The combustion analysis shows that organic compounds contain 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is empirical formula? If the molecular mass of this compound is 110.15 g mole^{-1} then calculate molecular formula of given organic compound. (Ans: C_3H_3O, $C_6H_6O_2$)***

Solution:

Element	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	65.44	$\frac{65.44}{12} = 5.45$	$\frac{5.45}{1.82} = 3$	C_3H_3O
H	5.50	$\frac{5.50}{1.008} = 5.45$	$\frac{5.45}{1.82} = 3$	
O	29.06	$\frac{29.06}{16} = 1.82$	$\frac{1.82}{1.82} = 1$	

Thus the empirical formula is C_3H_3O

To determine the molecular formula, first calculate the empirical formula mass.

Empirical formula mass of C_3H_3O $= 12 \times 3 + 1.008 \times 3 + 16 \times 1 = 55.05 \text{ g mol}^{-1}$

Molecular (or molar) mass of the compound $= 110.15 \text{ g mol}^{-1}$

$$n = \frac{\text{molecular mass of compound}}{\text{empirical formula mass of compound}} = \frac{110.15}{55.05} = 2$$

Thus Molecular formula $= n$ (empirical formula)

$= 2\,(C_3H_3O)$

$= \boxed{C_6H_6O_2}$

(iv) ***What is meant by the term chemical shift of a particular proton in NMR spectroscopy? Also draw the splitting pattern of protons in NMR spectrum of ethyl alcohol.***

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(v) ***Discuss the general principle and instrumentation of Atomic Emission Spectroscopy.***

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What is the basic principle of Atomic Absorption Spectroscopy? Describe the instrumentation used.

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...t is the basic principle of Mass Spectrometer? How does it work?

...e 513

TEST YOUR SKILLS
Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.

(i) A .... is an instrument which allows radiation to interact with sample of chemical and analyze the changes
(A) combustion chamber **(B) spectroscope** (C) Mass spectrum (D) HPLC - MS

(ii) Infrared radiation makes the bonds of molecule to ....
(A) excite (B) rotate **(C) vibrate** (D) None

(iii) .... radiation excites the electrons from lower energy level to highest level.
(A) ultraviolet (B) Visible (C) Microwaves **(D) both a & b**

(iv) .... involves radio waves
(A) Nuclear magnetic resonance (B) Electron spin resonance
(C) Mass Spectrometry (D) both a & b

(v) IR absorption is used to identify bonds and .... in an organic compound
(A) no of carbon atoms **(B) functional groups** (C) rotation (D) none of these

(vi) Which of following techniques does not involve electromagnetic radiation?
(A) NMR Spectroscopy (B) Infrared Spectroscopy
(C) Mass Spectroscopy (D) All of these

(vii) Which of the following is used as source of visible radiations?
(A) Tungsten filament lamp (B) Deuterium discharge lamp
(C) Hydrogen discharge lamp (D) none

(viii) In IR spectrum of propanone, strong peak is at about 1720 cm⁻¹ which refers to .... bond
(A) C – C bond (B) C – H bond (C) C = O bond (D) both a & c

(ix) In IR spectrum of propanone which absorption at .... refers to C – H bond
(A) $1600\ cm^{-1}$ (B) $2500\ cm^{-1}$ **(C) $3000\ cm^{-1}$** (D) $1900\ cm^{-1}$

(x) Useful and interesting region of IR spectrum is the region above ....
(A) $1500\ cm^{-1}$ (B) $2000\ cm^{-1}$ (C) $3000\ cm^{-1}$ (D) $3400\ cm^{-1}$

(xi) A solution of titanium (III) chloride appears violet, it absorbs which region of spectrum?
(A) green (B) yellow **(C) green - yellow** (D) Red

(xii) In mass spectrometry, ions with .... mass / charge ratio will be deflected smaller
(A) smaller **(B) greater** (C) particular (D) None

(xiii) The position of ultraviolet – visible absorption band is commonly expressed by
(A) Wave length (B) Wave Number (C) both (D) None

(xiv) Why do transition metal compounds show colour
(A) due to incomplete d- orbital's (B) due to metallic nature
(C) because of excitation of molecule (D) all of these

(xv) HCl molecule absorbs IR radiation of frequency ....
(A) 7.21×10^{13} Hz (B) 6.2×10^{13} Hz (C) 5.5×10^{14} Hz (D) 1.6×10^{15} Hz

(xvi) .... is chosen as NMR reference
(A) ethyl benzene (B) ethanol (C) H_2O **(D) tetramethylsilane**

(xvii) Which of the following species is detected in mass spectrometer?
(A) Radicals **(B) Positively charged species**
(C) Neutral molecules (D) All of these

(i) SUBJECTIVE

(ii) Time: 2:35 Hours **Total Marks Section B and C: 68**

(iii) Section – B (Marks 42) (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

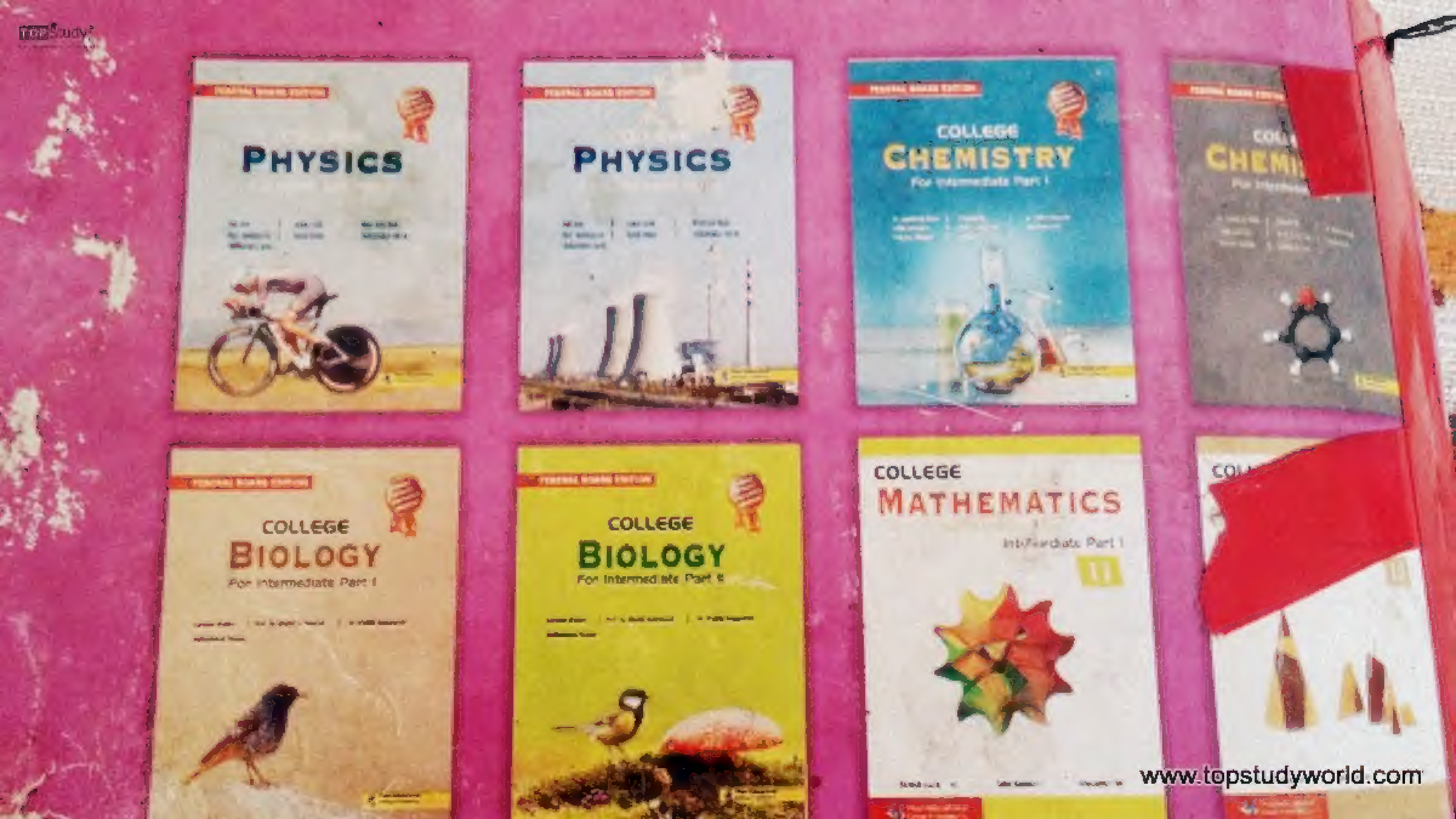
(i) (a) Differentiate between Qualitative & Quantitative analysis. (2)
(b) Define Analytical chemistry. (1)
(ii) (a) Define Spectroscopy. (1)
(b) Describe different types of Specter scopy. (2)
(iii) Describe characteristic significance of IR Spectroscopy. (3)
(iv) How does IR spectroscopy examplain type of bonds & functional group in case of prop none. (3)
(v) (a) Why transition metal compounds are coloured. (1)
(b) What happens when radiation strokes a substance? (2)
(vi) Describe why methylene blue is blue in colour? (3)
(vii) Aqueous solution of Titanium (III) chloride is violet in color. Explain the phenomena behind this. (3)
(viii) What is significance of NMR Spectro scopy?
(ix) (a) What is NMR Referena? (1)
(b) Why strutting of peals occur in NMR spectrum. (2)
(x) (a) How emission spectroscopy is applied in metallurgy? (1.5)
(b) How lubricant oil can be analysed by emission spectroscopy. (1.5)
(xi) (a) Describe the basic principle of Atomic Absorption Spectroscopy. (2)

(b) Which type of elements and samples are analyzed by AAS (1)
(xii) (a) Name main steps involved in mass Spectrometer (1.5)
(b) How sample is ionized in mass Spectrometer (1.5)
(xiii) How ion detector works in mass Spectrometer (3)
(xiv) Describe basic principle of chromatography (3)
(xv) (a) What is LC – MS? (1)
(b) Describe applications of GCMS (2)
(xvi) How will you distinguish between (3)
(a) Pentanone and b) Rentanone by using mass spectra. (3)
(xvii) Differentiate between atomic absorption Spectroscopy and atomic commission Spectroscopy (3)
(xviii)(a) What is wavelength of IR & UV (2)
(b) Which colour of visible light clear methylene blue absorb? (1)
(xix) (a)What is drawback of combustion analysis? (1)
(b) Name modern methods of analysis (2)

Section – C

Note: Attempt any TWO questions. All questions carry equal marks. (2 ×13=26)

1. (a) How molecular formula of organic compound is determined by combustion analysis? (5)
(b) An organic compound consist of C, H, O was subjected to combustion analysis 0.5438 g of compound g are 1.039 g of 0.6369 g of H_2O determine empirical formula of compounds (4)
(c) How different types of radiation interact with chemicals (4)
2. (a) Define IR Spectroscopy. How IR spectroscopy is applied to analyze different compounds (5)
(b) Describe Spin – spin coupling in NMR Spectroscopy (4)
(c) Explain advantages & Disadvantages of AES (4)
3. (a) Explain instrumentation & working of Mass Spectrometer (5)
(b) Describe application of AAS (4)
(c) How chromatography and MS can be helpful in analysis if combined together (4)
4. (a) Explain chemical shift of particular proton in NMR spectroscopy using example (5)
(b) How analytical chemistry benefits in field of Forensic sciences (4)
(c) Discuss application of Atomic emission spectroscopy (4)


PHYSICS
PHYSICS
COLLEGE
CHEMISTRY
For Intermediate Part I
COLLEGE
BIOLOGY
For Intermediate Part I
COLLEGE
BIOLOGY
COLLEGE
MATHEMATICS
Intermediate Part I
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